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PHILOSOPHICAL TRANSACTIONS.

I. *A Memoir on the Theory of Mathematical Form.*[*]

By A. B. KEMPE, *M.A., F.R.S.*

Received May 18,—Read June 18, 1885.

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[*] In accordance with criticisms and suggestions of the referees, an alteration has been made in the title of the memoir, and certain sections towards the end have been omitted. There is consequently a slight want of complete correspondence between the memoir and the abstract given in the Proceedings, vol. 38, p. 393—A. B. K.

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Scope of the Memoir.

1. My object in this memoir is to separate the necessary matter of exact or mathematical thought from the accidental clothing—geometrical, algebraical, logical, &c.—in which it is usually presented for consideration; and to indicate wherein consists the infinite variety which that necessary matter exhibits.

2. The memoir is confined to the exposition of fundamental principles, to their elementary developments, to their application to such a variety of cases as will vindicate their value, and to a description of some simple and uniform modes of putting the necessary matter in evidence. I have been unable to ascertain that the principles here set forth have been previously formulated.

Fundamental Principles.

3. Whatever may be the true nature of things and of the conceptions which we have of them (into which points we are not here concerned to inquire), in the operations of reasoning they are dealt with as a number of separate entities or *units.*

4. These units come under consideration in a variety of garbs—as material objects, intervals or periods of time, processes of thought, points, lines, statements, relationships, arrangements, algebraical expressions, operators, operations, &c., &c., occupy various positions, and are otherwise variously circumstanced. Thus, while some units are incapable of being distinguished from each other, others are by these peculiarities rendered distinguishable. For example, the angular points of a square are distinguishable from the sides, but are not distinguishable from each other. In some instances where distinctions exist they are ignored as not material. Both cases are included in the general statement that some units are distinguished from each other and some are not.

5. In like manner some *pairs* of units are distinguished from each other, while others are not. Pairs may in some cases be distinguished even though the units

composing them are not. Thus the angular points of a square are undistinguishable from each other, and a pair of such points lying at the extremities of a side are undistinguishable from the three other like pairs, but are distinguished from the two pairs formed by taking the angular points at the extremities of the diagonals, which pairs again are undistinguishable from each other. Further, a pair ab may sometimes be distinguished from the pair ba though the units a and b are undistinguished. Thus, in fig. 1 the three black spots a, b, c, are all undistinguished from each other, each has an arrow proceeding to it and an arrow proceeding from it, but the pair ab is distinguished from the pair ba, for an arrow proceeds from a to b, but none from b to a.

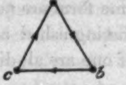


Fig. 1.

6. It will be convenient to speak of ab and ba as different *aspects* of the *collection* of two units a, b. Here the terms "aspect" and "collection" are each to be understood as referring to two separate units, and not to those units regarded in the aggregate as a single unit.

7. Again, there are also distinguished and undistinguished *triads, tetrads, . . . m-ads, . . . n-ads . . .*; every m-ad being, of course, distinguished from every n-ad. Just as we may have ab distinguished from ba, though a is undistinguished from b, so we may have an n-ad $pqrst \ldots uv$ distinguished from $qusvt \ldots rp$, though the units p, q, r, s, &c., are all undistinguished from each other, and further, though their pairs are also undistinguished, as likewise their triads, &c. Here $pqrst \ldots uv$ and $qusvt \ldots rp$ will be termed, as in the case of pairs, different *aspects* of the *collection* $p, q, r, s, t, \ldots u, v$; the term "collection" being understood to refer to a number of separate units without reference to the various "aspects" of the collection. Different aspects of the same collection of n units will be regarded as different n-ads.

8. The terms "pair," "triad" . . . "n-ad," "collection," "aspect" will always be understood to refer to two, three, n, &c., units, and never to aggregations of units considered as a single unit. Pairs, triads, n-ads, collections, aspects may, of course, be regarded as units, but when they are so regarded the fact will be distinctly pointed out.

9. Every collection of units has a definite *form* due (1) to the number of its component units, and (2) to the way in which the distinguished and undistinguished units, pairs, triads, &c., are distributed through the collection. Two collections of

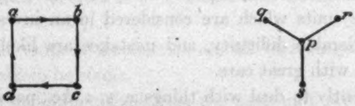


Fig. 2.

the same number of units but having different distributions will be of different forms. Thus the two tetrads a, b, c, d, and p, q, r, s, of fig. 2, contain the same number (four) of unit spots, but they are of different forms; for a, b, c, d are all undistinguished from each other; while q, r, s, though undistinguished from each other, are all distinguished from p. The distribution of the distinguished and undistinguished pairs and triads is also obviously different in the two cases. The word "form" will in this memoir be always employed in the sense here indicated.

10. Two collections of units which are undistinguished are of the same form, but two collections which are of the same form are not necessarily undistinguished; there may be the same distribution of distinguished and undistinguished units, pairs, &c., in each, while the units, pairs, &c., of one are all distinguished from the units, pairs, &c., of the other.

11. Each of the forms which a system of any number n of units can assume, owing to varieties of distribution, is one of a definite number of possible forms, and the peculiarities and properties of the collection depend, as far as the processes of reasoning are concerned, upon the particular form it assumes, and are independent of the dress, geometrical, algebraical, logical, &c., in which it is presented; so that two systems which are of the same form have precisely the same properties, although the garbs in which they are severally clothed may, by their dissimilarity, lead us to place the systems under very different categories, and even to regard them as belonging to "different branches of science."

12. It may seem in some cases that other considerations are involved besides "form," but it will be found on investigation that the introduction of such considerations involves also the introduction of fresh units, and then we have merely to consider the form of the enlarged collection.

13. In order to put form in evidence some "accidental" clothing is of course necessary; if, however, we employ more than one species of clothing, each species being uniform and suited to forms of every kind, the likelihood of its accidental nature being overlooked will be reduced to a minimum.

Units.

14. The units which we have to consider exhibit endless variety; thus we may have a material object dealt with as one unit, a quality it possesses as another, a statement about it as a third, and a position it occupies in space as a fourth. The task of specifying the units which are considered in an investigation may in some cases be one of considerable difficulty, and mistakes are likely to occur unless the operation is conducted with great care.

15. We have frequently to deal with things x, y, z, &c., pairs, &c., of those things, the differences between which depend on the existence or non-existence of certain circumstances, or upon taking into account or ignoring certain circumstances. Thus we may apparently have collections of units x, y, z, &c., which are at one time t, when

one state of things exists, of one form, and at another time t' of another form. This is, however, not so; the form of a collection is absolutely invariable. The apparent alteration of form arises from overlooking the fact that the units dealt with are not x, y, z, &c., but (x at time t), (y at time t), &c., (x at time t'), (y at time t'), &c. The unit (x at time t) may be quite different from (x at time t'). Where there is only one alternative t, the collection (x at time t), (y at time t), (z at time t), &c., is of the same form as the collection x, y, z, &c., and it matters not which is the collection dealt with.

16. Aggregations of those things which, in a symbolical representation of the units considered in any case, are already represented as units, must not be supposed to be sufficiently represented without additional symbols, but must each be represented by a distinct symbolical unit. An aggregation of things is, as far as the processes of reasoning are concerned, a mere unit, and must be so dealt with.

17. While it is important that a unit should be represented and dealt with as a unit, it is equally important that we should not be misled by our modes of thought and consequent use of language into regarding a number of distinct units as one only. A collection of units must in a symbolical representation be represented as a single unit where it is so regarded; but where the word "collection" is used, as it is here (sec. 8), merely to "denote" or mark off a number of things each of which is considered as a distinct unit, we must be careful to represent each of those things by a distinct symbol.

Some Definitions.

18. Any collection of units which consists entirely of units selected from another collection will be termed a *component* of the latter. Any aspect of a component of a collection may also be spoken of as a component of the collection.

19. Two collections of units will be said to be *detached* if they have no component in common.

20. An n-ad which has one or more units in common with each of a number of collections will be said to be an n-ad *connecting* those collections; *e.g.*, the pairs which a single unit makes with the various units of a collection will be termed the pairs connecting the unit and the collection. An n-ad connecting n detached collections has one unit and one only in common with each. If A, B, C, D, ... be collections of which a, b, c, d, . . . are component units respectively; when an n-ad connecting A B C D . . . is spoken of, it must be understood that an n-ad such as $a\ b\ c\ d$ . . . is meant, and not one such as $b\ d\ c\ a$ . . ., which will be spoken of as connecting B D C A . . .

21. If the component units of a collection are all undistinguished from each other the collection will be said to be *single.*

22. Units which are undistinguished from the same unit are undistinguished from each other; thus if a collection of units is not single it consists of two or more detached single collections, and will be termed a *double, treble, &c.*, collection, according to the number of component single collections which it contains.

23. Just as collections of units break up into single collections of undistinguished units, so collections of pairs break up into single collections of undistinguished pairs, and, generally, collections of n-ads into single collections of undistinguished n-ads.

24. Differences between the various units, pairs, &c., of a collection may be termed the *internal* differences of that collection. Differences between the various units, pairs, &c., of a collection A and the units, pairs, &c., of a detached collection may be said to be *external* to A.

Systems.

25. If every component unit of a collection is distinguished from every unit which is detached from the collection, the collection will be termed a *system.*

26. Every collection of units is a component of some system.

27. The whole collection of units which come under consideration in any inquiry is a system; for the units are distinguished from all others by being the only ones considered.

28. The n-ads of one single system of units are distinguished from all those of any other single system of units, and from all the n-ads connecting any two systems of units. The connecting n-ads of any n systems of units are distinguished from those of any other n systems of units, and themselves break up into single systems of n-ads.

29. The units of a single system of units must be dealt with as a whole; for, as they are undistinguished from each other, no definition can be given of, or remark made about, one which is not equally applicable to each of the others. Each can only be spoken of as "one of" the units of the system. A similar observation applies in the case of single systems of pairs, triads, &c.

30. Many systems of units are defined by stating that certain of their components constitute a system. It must be borne in mind that such a statement does not mean that the components are undistinguished from each other, but merely that they are distinguished from all others; the system of components may be a multiple one. It is by no means unnecessary to emphasize this, as we are prone to assume that the mode of classifying things is that of putting like things into the same class, rather than that of putting unlike things into different classes.

31. The distribution of the various distinguished and undistinguished components of a system is regulated by definite laws; so that a knowledge of the mode of distribution of some only of the distinguished and undistinguished components may determine the form of the system. There are in general several ways in which the form of a given system may be thus determined, and accordingly various different definitions of the same system may be adopted.

32. For the statement of some of the properties of a system S it may be necessary to have the form fully defined; in the case of others this may not be necessary, it being sufficient to state that certain components are distinguished, without asserting anything as to others, *i.e.*, to state that certain components constitute a system,

without asserting whether the system be single or multiple. The result of this may of course be that we deal with different units at different stages of the investigation of S (secs. 126 *ff*).

33. Systems are frequently more readily dealt with when regarded as components of more extensive systems. Much ingenuity has been expended on the discovery of systems, the addition of which to the particular system under consideration may assist in its investigation. It is to this that the existence of such units as substitutions, quarternions, quadrates, &c. (as to some of which I shall have to speak presently), is due. We shall see that we can always, by the addition of a proper system to any given system, completely define the latter by merely indicating the mode of distribution of certain pairs (secs. 81, 82).

34. Notwithstanding the great assistance derived from the use of added systems, much reluctance is exhibited in employing them unless they can be shown to have their representatives in nature, *i.e.*, unless "accidental" clothing can be found to fit them. The objections raised to symbolical methods which cannot be "interpreted" are strong evidence of the fact that the accidental nature of much that comes under our consideration is not really appreciated.

35. It is by no means unnecessary to state that the form of a system is independent of the particular method of defining it which we adopt; and that because it is easier to define a system by adding fresh units, it does not owe its form to the existence of those units.

36. The system which is the actual subject of investigation in an inquiry may be termed the *base* system; those systems which are added for the purpose of assisting in the investigation being termed *auxiliary* systems.

Heaps.—Graphical Representation of Units.

37. There are two forms of systems of n units the consideration of which properly precedes that of all others. The one is that of a system which consists of n units, each of which is distinguished from each of the others, so that every component s-ad is distinguished from every other component s-ad for all values of s from 1 to n. A system of this form I shall term a *discrete heap.*

38. The other is that of a system of n units which is such that every component s-ad is undistinguished from every other component s-ad for all values of s from 1 to n. A system of this form I shall term a *single heap.*

39. A discrete heap may be graphically represented by a number of small separated circles each containing a different letter (fig. 3). The letters render the *graphical units* distinguishable from each other.

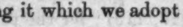


Fig. 3.

40. A single heap may be graphically represented by a number of small separated circles each containing the same letter. (Fig. 4.)

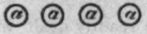


Fig. 4.

41. Differences arising from the positions of the graphical units on the paper on which they are drawn are always to be disregarded. Where positions are considered, they must be represented by separate graphical units.

42. Where there is occasion to employ letters outside and adjacent to the graphical units for purposes of reference, differences arising from the use of such letters are also to be ignored. (Sec. 173.)

43. In every system of n units other then a discrete or single heap, some s-ads are distinguished from each other and some are not, for all or some values of s from 1 to n. Thus every form which a system of n units can assume may be regarded as either that of a discrete or single heap or as intermediate between the two.

44. There are systems of n units of other forms than those of discrete and single heaps which can be represented by means of graphical units alone. These consist of one or more detached independent single heaps. The term "independent" will be fully explained presently (secs. 117, 118); for the present it will be sufficient to state that two independent systems are such as can be graphically represented on separate sheets of paper, without the employment of symbols on either sheet relating to those on the other.

45. A system of s independent detached heaps will be termed an s-tuple heap. Fig. 5 represents a treble heap of seven units.

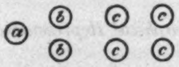


Fig. 5.

46. A discrete heap of n units is an n-tuple heap of n units.

47. The number of different forms which a heap of n units can assume is the same as that of the partitions of n.

48. It will in some cases be convenient, instead of employing circular graphical units distinguished by internal letters, to use coloured graphical units, or black spots of different sizes, or graphical units of various shapes.

49. Where graphical units are employed alone, like units will represent undistinguished units, but in the case of forms other than heaps it will be necessary to employ means to distinguish pairs, &c., and these may cause like graphical units to be distinguished from each other. No general inference must therefore be drawn from the use of like and unlike graphical units other than that unlike units represent distinguished units.

Pairs.—Graphical Representation.

50. There are three different forms of pairs; viz., if a, b be two units, we can have:—

(1) a distinguished from b, and therefore also ab distinguished from ba;

(2) a undistinguished from b, but ab distinguished from ba;

(3) a undistinguished from b, and ab undistinguished from ba.

51. The two units in case (1) belong to different single systems, and thus the pair is a pair connecting two single systems.

52. In cases (2) and (3) both units belong to the same single system, and the pairs are components of that system. The units in case (2) may be said to form an *unsymmetrical* pair, those in case (3) being said to form a *symmetrical* pair. It will be convenient in speaking of undistinguished unsymmetrical pairs ab, cd, to say that ab and cd are *of the same polarity*, and that ab and dc are *of opposite polarities.* Of course in this case ab and ba are of opposite polarities. In the case of a symmetrical pair e, f, ef and fe will be of the same polarity.

53. The expression "unsymmetrical" may also be applied to pairs falling under case (1). We may also in the case of such pairs say that ab and cd if undistinguished are of the same polarity, ab and dc of opposite polarities.

54. If in a diagram consisting of a number of graphical units, some pairs of those units are joined by plain lines or links, as in fig. 6, while others are not so joined, the pairs will be divided into two systems. Pairs which are thus joined by links will not be necessarily undistinguishable, nor will pairs which are not joined by links be necessarily undistinguishable, but we merely have pairs which are joined by links distinguished from pairs which are not so joined. Thus the two systems into which the pairs are divided may each be either a single or multiple system.

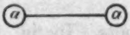


Fig. 6.

55. A large number of systems may be completely defined by diagrams consisting of graphical units and links only. We have already seen that an extensive class of systems may be represented by diagrams consisting of different sorts of graphical units only; there are also systems which may be fully defined when we indicate by links a dichotomy of their component pairs, without defining further what units are distinguished and what are not. Thus the system of fig. 7 must be a discrete

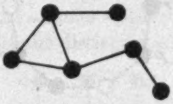


Fig. 7.

heap, each graphical unit admitting of separate definition. By the use of links in conjunction with graphical units of different sorts the number of representable forms is greatly increased. I shall give in the following four sections some examples of forms which may be represented by the use of graphical units and links.

56. Figs. 8 and 9 illustrate the fact that a system may be defined in various ways;

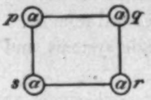


Fig. 8.

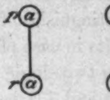


Fig. 9.

they represent systems of the same form. Pairs which are not joined by links in fig. 8 are joined in fig. 9, and *vice versâ*.

57. I give the systems of figs. 10 and 11 as examples of two varieties of single

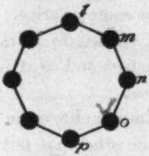


Fig. 10.

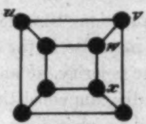


Fig. 11.

systems of the same number of units. In fig. 10 there are four sorts of pairs of which *lm*, *ln*, *lo*, *lp*, are types. In fig. 11 there are only three sorts, of which *uv*, *uw*, and *ux*, are types. It may be noticed that in each case the linked pairs compose a single system; while the unlinked pairs in the former case compose a treble system, in the latter a double one.

58. Fig. 12 is an example of a triple system containing unsymmetrical pairs of both

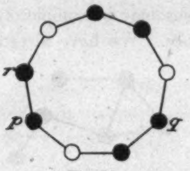


Fig. 12.

sorts. We have p, q an unsymmetrical pair composed of two undistinguished units, and p, r an unsymmetrical pair composed of two distinguished units.

59. The single system shown in fig. 13 is one of considerable interest; it is that dealt with in the case of the theorem that if two coplanar triangles are coaxial they

are also copolar (Theorem (1), sec. 357). The graphical units may be taken to represent either the ten straight lines of the theorem, or the ten points of intersection;

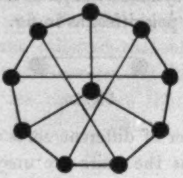


Fig. 13.

the form is the same in either case. Taking the former case, the pairs of graphical units which are joined by links correspond to pairs of lines whose points of intersection are points other than the ten considered in the theorem. It should be noticed that the two systems into which the pairs are divided (linked and unlinked), are each single.

60. We shall see (secs. 81, 82), that by the addition of units to any system S, *i.e.*, by regarding S as a component of a more extensive system, we can represent the form of S by the use of graphical units and links only. It will, however, be convenient in many cases to employ some further devices which will enable us, without employing additional graphical units, to represent forms which could not be exhibited by the use of plain links only.

61. Thus we may have lines of various sorts joining two graphical units, viz., dotted, wavy (fig. 14), red, blue, &c., in addition to links, which will always be understood to be plain lines. Pairs joined by unlike lines will be, as in the case of links, distinguished from each other.

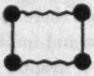


Fig. 14.

62. Where a pair is unsymmetrical an arrow-head or barb may be added to the link or other line joining the two graphical units which represent the pair (fig. 15). The arrow-head has the effect of making *ab* distinguished from *ba*. In the fig. the arrow-heads make *ab* distinguished from *fe*, but not from *ef*. The relative directions of the arrow-heads in the case of pairs joined by unlike lines are immaterial. It is

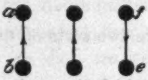


Fig. 15.

unnecessary to add an arrow-head in the case of a pair of distinguished units; the difference between the graphical units indicates the absence of symmetry.

63. We may in some cases of symmetrical pairs instead of employing a single line, use two barbed lines of opposite polarities, as in fig. 16.

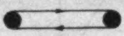


Fig. 16.

64. In place of using a number of different sorts of lines, we may use plain lines, barbed or unbarbed according as the pairs are unsymmetrical or symmetrical, with letters alongside of them; like letters being used where otherwise like lines would be used, and unlike where unlike lines would be used (fig. 17). Though this method is not so good as the previous one as regards its power of enabling us to visualize the

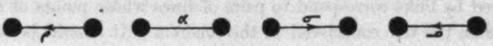


Fig. 17.

systems represented, it has distinct advantages for purposes of description, as we can denote pairs of different sorts by the annexed letters, the sorts (sec. 84) of which denote the sorts of the pairs.

65. If σ denotes an unsymmetrical pair *ab*, we may denote the pair *ba* by $\rotatebox[origin=c]{180}{σ}$; or, as this is in some instances awkward, by σ' where $(\sigma')'=\sigma$.

66. Although, as we have seen, it is in many cases unnecessary to draw lines connecting all pairs of graphical units in order to completely define a system (secs. 55–59), it may in some cases be desirable to do so, especially where we wish to show how many different sorts of pairs there are under consideration. In such cases we may connect like pairs by like lines and unlike by unlike lines. Thus the diagram of fig. 18, which completely defines a system of six units, may be completed as in fig. 19 so as to show that there are two sorts of unsymmetrical pairs and one sort of symmetrical pairs.

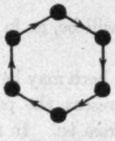


Fig. 18.

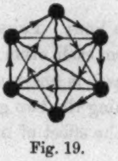


Fig. 19.

67. In general, in diagrams in which lines other than links are employed, either in conjunction with links or not, like pairs of graphical units will be joined by like lines.

68. It can readily be shown that every form which admits of representation by

means of graphical units and lines of different sorts, can, by the introduction of additional or *auxiliary* graphical units, be represented by means of graphical units and links only. It will be convenient for the purpose of description to suppose that the lines of different sorts are of different colours. In the place of any red line substitute a red unit (*i.e.*, one coloured red, instead of having a letter inside), this unit being connected by two links to the two units which were joined by the red line (fig. 20). Effect this change in the case of all the red lines; and

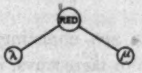


Fig. 20.

similarly in the place of blue, yellow, &c., lines, substitute blue, yellow, &c., units, joined by links to the units which were connected by the several coloured lines. The red units and links will have precisely the same effect in rendering pairs distinguishable as the red lines had. We may, if we please, substitute letters for the various colours in the added units, and so obtain a diagram consisting of graphical units and links, representing a collection of which the original one is only a component. This component is, however, of the same form as before.

69. In the case of an unsymmetrical pair, pq, of undistinguished graphical units which would ordinarily be joined by a barbed line, we must have two additional undistinguished graphical units in some cases, as in fig. 21, where u, v are the auxiliary units.

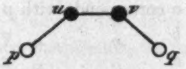


Fig. 21.

70. In the case of unsymmetrical pairs of distinguished units we have seen that no barbs are necessary (sec. 62), and we need therefore only one additional graphical unit, as in sec. 68.

71. All systems of which the forms are determined by the distinguishableness and undistinguishableness of units and pairs only, may be represented by the methods we have been considering. But there are also systems, the forms of which are not so determined, but depend upon the distinguishableness and undistinguishableness of triads, tetrads, &c. Such systems may at first sight require other expedients for their graphical representation, but we shall see, as already stated (secs. 33, 60), that these are not necessary.

72. Diagrams such as those we have been discussing may come under our consideration in other ways than as representing graphically systems of different forms. In such cases it must not be assumed that the units under consideration

are the small circles, or only those; in general this will not be so; the units may be the links, or the *ways* in which a number of small circles or spots can be connected by links, &c. If we ascertain exactly what the units really dealt with are, we may construct a graphical representation of the system they constitute, and this may be of a very different character from that of the diagram from which it is derived.

Aspects.

73. If two collections of units are undistinguished, they may be regarded as corresponding to each other in one or more ways, in each of which correspondences to each unit, and therefore to each pair, triad, &c., of one collection there corresponds in the other a counterpart unit, pair, triad, &c., undistinguished from the former in dress or other circumstance. In any one of these correspondences, two corresponding units are regarded as occupying corresponding places, or, as we may express it, places of the same *sort*. Furthermore, each of the corresponding units is regarded as belonging to one or the other of the two collections, each of which is regarded also in the aggregate as a single unit.

74. Now the unit A which is dealt with when we thus regard a unit a as occupying a place of a particular sort g in a particular collection, is a different unit from a; it may be called an *aspect* of a.

75. Thus when we consider a correspondence of two undistinguished collections $a, b, c, d, \ldots$ and $p, q, r, s, \ldots$ where

a corresponds with p
b " " q
c " " r

and so on, we deal with a collection of units A, B, C, D, ... P, Q, R, S, ... where any unit R is the unit arrived at by considering the unit r as occupying a place of a particular sort, the unit C being that arrived at by considering the unit c as occupying a place of the same sort; and similarly in the case of the other corresponding units. Each of the collections A, B, C, D, . . . and P, Q, R, S, ... is an *aspect*, the former of the collection $a, b, c, d, \ldots$ and the latter of the collection $p, q, r, s, \ldots$ We also regard A, B, C, D, . . . in the aggregate as a single unit V, which may be termed a *unified aspect* of $a, b, c, d, \ldots$ and so also in the case of P, Q, R, S, . . .

76. The collections A, B, C, D, . . . and P, Q, R, S, . . . may be different aspects of the same collection $l, m, n, o, \ldots$, as a collection may be *self-correspondent*, and the number of units $a, b, c, d, \ldots$ be accordingly the same as that of the number of sorts of places considered.

77. We may have a number of undistinguished collections, each of n units, all corresponding to each other. If there be m such collections, in any correspondence in

which they all correspond we have *mn* unit aspects such as A, *n* sorts of places, and each sort of place occupied by *m* units.

78. A, the aspect of *a* in a correspondence, bears definite relations (sec. 79) to three other units, viz. :—

(1.) *a* of which it is an aspect.

(2.) The unified aspect V arrived at by regarding as a unit the aspect of which it is a component.

(3.) The sort *g* of the place *a* occupies in the correspondence.

79. The "definite relations" of the preceding section consist merely in this, viz., that the pairs which A makes with *a*, V, and *g*, are all distinguished from all the other pairs which A makes with other units. (See secs. 143 *ff*, on *Associates*.)

80. The tetrad A, *a*, V, *g*, may be graphically represented as in fig. 22; the graphical unit A being joined to no other graphical units besides *a*, V, and *g*. Since the units A, *a*, V, and *g*, are obviously distinguished from each other, the graphical units are made so also.

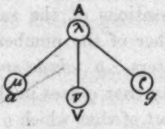


Fig. 22.

81. It appears, then, that in studying the form of a system S by means of correspondences of undistinguished components, we really regard S as a component of a more extensive system, containing

(1.) the system S;

(2.) the system X composed of units which are conceived of as sorts of places;

(3.) the system Y composed of units which are conceived of as unified aspects of all the various component collections of S;

(4.) the system Z composed of units which are conceived of as aspects of single units of S.

The pairs connecting Z and the joint system S, X, Y, break up into two systems, graphically represented by linked and unlinked pairs of graphical units respectively.

82. A graphical representation in which the units of S, X, Y, Z, are all represented by graphical units, and links connecting the graphical units are drawn in the manner indicated in the last two sections, fully defines the form of S, as it completely indicates what components are undistinguished and what are not. Such a graphical representation is sometimes termed a "linkage," so that we may say that every system may be graphically represented by a linkage (secs. 194, 195).

83. The system Y was described in sec. 81 as consisting of unified aspects of *all* the component collections of S, *i.e.*, the component pairs, triads, &c. It is, however, unnecessary so far as defining the form of S is concerned that this should be so. We shall see that it is sufficient that Y should include a unified aspect V of the whole system S, and all other unified aspects of S which are undistinguished from V (secs. 194, 195).

Letters, their Sorts and Positions.

84. Let us now turn aside to consider certain points with regard to the representation of units by letters. Any letter admits of being repeated as often as we please; each repetition being one of a number of letters of the same *sort.* When in common parlance we speak of letters *a*, *b*, *c*, *d*, &c., we are really referring, not to the letters themselves, but to their sorts. Each letter (not sort of letter) occupies a different position on the paper on which it is written or printed; as in the case of the letters, we have a number of positions of the same sort, each called "the same position" with reference to another of the number. For example, if we have two arrays of the same number of letters, *e.g.*, *abcde* and *pqrst*, we say that "*b* occupies the *same position* in the first array that *q* does in the second," meaning that the sort of the position *b* occupies is the sort of that which *q* occupies.

85. The sorts of the letters and the sorts of the positions are both dealt with as units. Further, we regard each letter as belonging to a particular collection regarded in the aggregate as a single unit, say a *unified collection.*

86. Thus a letter bears definite relations to

(1.) its sort;

(2.) the unified collection to which it belongs;

(3.) the sort of its position.

Representation of Aspects of Collections by Arrays of Letters.

87. Thus we have an exact copy in a different dress of the state of things considered in secs. 73–83. If then we represent

(1.) the units of any collection by the sorts of letters; we may represent

(2.) the sorts of places occupied by those units in a correspondence with an undistinguished collection by the sorts of the positions of the letters;

(3.) an aspect of the collection by a collection of letters in sorts of positions;

(4.) unified aspects by unified collections of letters;

(5.) aspects of single units by single letters.

88. Taking, then, arrays as our collections of letters, an aspect may be represented thus *abcdef* . . . . . (*i.e.*, in the manner adopted in sec. 7), where the order of the letters is to be regarded as material to this extent, viz., that though the aspect which is

represented by *abcdef* . . . . might equally well be represented by *bdacfe* . . . . , yet, if this be done, the aspect originally represented by *bdacfe* . . . must be represented by *dcbaef* . . . , and that originally represented by *pqrstu* . . . by *qsprut* . . . . , and similarly in the case of other aspects and other transpositions of the sorts of the positions occupied by the letters in the arrays. Whatever change be effected in the order of the letters in one array, a precisely similar change must be made in the order of the letters in each of the other arrays of the same number of letters. The relative order in arrays of different numbers of letters is immaterial, as such arrays represent collections of different numbers of units which are therefore distinguished, and are not regarded as corresponding.

Elementary Properties of Aspects.

89. The symbols $\succ\!\!-\!\!\prec$ and $\longleftrightarrow$ will be used to represent "is undistinguished from" and "is distinguished from" respectively; and such expressions as "let $a \succ\!\!-\!\!\prec b$" must be read, "let a be undistinguished from b"; and similarly in other cases.

90. Symbols, such as a, b, c, d, in which commas separate the letters, will always be supposed, as heretofore, to represent a collection of units without reference to particular aspects, the order of the letters being accordingly supposed to be immaterial.

91. A statement such as *abcd* . . . . $\succ\!\!-\!\!\prec$ *pqrs* . . . . implies that the components represented by taking corresponding letters on each side of the $\succ\!\!-\!\!\prec$ are undistinguished; *e.g.*, $bc \succ\!\!-\!\!\prec qr$. A statement such as *abcd* . . . . $\longleftrightarrow$ *pqrs* . . . . does not imply that $a, b, c, d, \ldots . \longleftrightarrow p, q, r, s, \ldots .$ for it is consistent with the statement that *abcd* . . . $\succ\!\!-\!\!\prec$ *srqp* . . . which implies that $a, b, c, d, \ldots \succ\!\!-\!\!\prec p, q, r, s, \ldots$

92. If *abcd* . . . $\succ\!\!-\!\!\prec$ *pqrs* . . ., then *bdca* . . . $\succ\!\!-\!\!\prec$ *qsrp* . . . ; and similarly in the case of any other transposition of letters.

93. If *pqrs* . . . be merely *abcd* . . . in a different order, so that we are considering two aspects of the same collection, and if we repeat on *pqrs* . . . the transposition by which it is derived from *abcd* . . ., we get another aspect which by the preceding section is undistinguished from *pqrs* . . ., and therefore from *abcd* . . .

94. If *abcd* . . $\succ\!\!-\!\!\prec$ *pqrs* . ., and if $l, m, n, o, \ldots$ be units other than $a, b, c, d, \ldots$, there must be units $w, x, y, z, \ldots$ other than p, q, r, s, such that *abcd* . . . *lmno* . . . $\succ\!\!-\!\!\prec$ *pqrs* . . . *wxyz* . . .

95. If *abcd* . . . $\longleftrightarrow$ *pqrs* . . . each collection having the same number of units, and if $l, m, n, o, \ldots$ be units other than $a, b, c, d, \ldots$ there cannot be any units $w, x, y, z, \ldots$ such that *abcd* . . . *lmno* . . $\succ\!\!-\!\!\prec$ *pqrs* . . . *wxyz* . . . .

96. Every collection of n units has $\underline{|n}$ aspects. If m aspects of the collection are undistinguished from each other, but are distinguished from all other aspects of the

collection, m must be a factor of $\underline{|n}$, and the aspects break up into $\frac{\underline{|n}}{m}$ systems, each consisting of m aspects.

97. It follows immediately from sec. 92 that if we write down the symbols *abcd* . . ., &c., representing any aspect and all other aspects which are undistinguished from it, and we transpose the letters of *abcd* . . . and make precisely the same transpositions in the case of the letters of the symbols representing the other undistinguished aspects, we shall get a collection of symbols of undistinguished aspects which may or may not be the same as the former.

98. If *abcd* . . . be an aspect of a whole system S of n units, so that all the aspects undistinguished from it are aspects of the whole system S, there being in all m undistinguished aspects, the different transpositions of sec. 97 will give us all the different systems of aspects of S referred to in sec. 96.

99. If the array of letters *abcd* . . . representing any aspect of a whole system S be given, and also those arrays representing all the other aspects of S which are undistinguished from *abcd* . . ., then the form of S is given; *i.e.*, if *pqrs* . . . be an aspect of any component collection of S, we know what other aspects of component collections of S are distinguished and what undistinguished from *pqrs* . . . For add letters to *pqrs* . . . until we get an array *pqrs* . . . *lmn* . . . representing an aspect of the whole system S. If this is not the same as one of the given arrays, transpose the letters of any one of the latter so that it becomes *pqrs* . . . *lmn* . . ., and make precisely similar transpositions in the case of each of the other given arrays. If now *wxyz* . . . $>\!\!\!-\!\!\!-\!\!\!<$ *pqrs* . . ., it follows from sec. 94 that there must be an aspect *wxyz* . . . *ijk* . . of the whole system S, such that *wxyz* . . . *ijk* . . . $>\!\!\!-\!\!\!-\!\!\!<$ *pqrs* . . . *lmn* . . . ; and if *wxyz* . . . $\longleftrightarrow$ *pqrs* . . . it follows from sec. 95 that there is no aspect *wxyz* . . . *ijk* . . . of the whole system S such that *wxyz* . . . *ijk* . . . $>\!\!\!-\!\!\!-\!\!\!<$ *pqrs* . . . *lmn* . . . ; *i.e.*, in the former case there must be a symbol *wxyz* . . . *ijk* . . . among the transposed arrays, in the latter case there can be no such symbol.

Tabular Representation of Systems.

100. A convenient mode of arranging the symbols *abcd* . . ., &c., representing a system of m undistinguished aspects of a whole system S of n units $a, b, c, d,$ . . . is

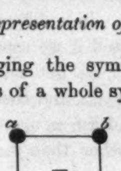


Fig. 23.

to place them one above another so that letters occupying "the same position" in the different rows may lie in the same column. For example, the system of fig. 23 may be represented thus :—

$$\begin{array}{ccccc} a & b & c & d & e \\ b & c & d & a & e \\ c & d & a & b & e \\ d & a & b & c & e \\ a & d & c & b & e \\ d & c & b & a & e \\ c & b & a & d & e \\ b & a & d & c & e \end{array}$$

101. The symbol thus arrived at, consisting of nm letters arranged in m rows and n columns, will be termed the *tabular representation* of S. Each of the nm letters will be termed an *element*.

102. The order of the rows is clearly immaterial. Any alteration in the order of the columns merely substitutes for one system of undistinguished aspects of S another system of undistinguished aspects of S, and any one of these systems of undistinguished aspects defines the form of S, thus the order of the columns is also immaterial. The material point is that certain elements are all in the same row, and certain elements all in the same column.

103. Each sort of letter represents a unit of S; each column regarded as a unit represents a sort of place; each row represents an aspect of S, or, regarded as a unit, a unified aspect of S; and each letter, or element, an aspect of a unit of S.

104. Any row R_2 may be regarded as derived from another row R_1 by a substitution of the letters of the row R_1. If the same substitution be effected upon any row R_3, we get a row R_4 which is also a row of the table.

105. The substitutions by which any row of the tabular representation of S is derived from another may be said to be *substitutions proper to S.*

106. If we confine our attention to certain rows and columns only of the tabular representation of S, we get a table which will be termed a *constituent* of the whole table. The order of the rows and columns will be disregarded in a constituent as in a complete table.

107. If $a \longleftrightarrow b$, a and b can never appear in the same column. Thus the columns break up into lots, each lot belonging to a single system.

108. If $a >\!\!\!-\!\!\!-\!\!\!< b$, then a appears in every column that b does, and b in every column that a does.

109. Generally if $abcd \ldots >\!\!\!-\!\!\!-\!\!\!< pqrs \ldots$ we have in the table a constituent $\begin{matrix} a\,b\,c\,d \ldots \\ p\,q\,r\,s \ldots \end{matrix}$, and if $abcd \ldots \longleftrightarrow pqrs \ldots$ we have no such constituent. Thus the forms of the various components can readily be ascertained from the table.

110. If we desire to consider the forms of portions only of a system, we may

confine our attention to such constituents as will exhibit the form. Thus in the case of sec. 100 the constituent $\begin{matrix} a & c \\ c & a \end{matrix}$ shows that the pair a, c is a symmetrical one.

111. A discrete heap will be represented by a table of one row; a single heap of n units by a table of $\underline{|n}$ rows; and a heap consisting of single independent heaps of $p, q, r, s, \ldots$ units respectively will have a table of $\underline{|p} \times \underline{|q} \times \underline{|r} \times \underline{|s} \ldots$ rows.

Correspondences of Undistinguished Collections.

112. The various correspondences of undistinguished collections are indicated by two-row constituents of the tabular representation of the system of which the collections are components.

113. If the two rows of the constituent contain like letters in different orders, the constituent will be said to indicate a *self-correspondence*, *i.e.*, a correspondence of a collection C with itself; and not with another collection (sec. 76). Any two-row constituent containing two complete rows of the table representing a system S will indicate a self-correspondence of S, and the table may accordingly be said to indicate the form of S by indicating all its self-correspondences.

114. If the two rows of the constituent representing a correspondence of C with itself contain like letters in the same order, the constituent will be said to indicate an *identical-correspondence* of C. The identical-correspondence may be regarded as included among the self-correspondences of C. The self-correspondence of a single unit is an identical-correspondence.

115. In general the table representing a system S will have rows which are partially alike, indicating that in some of the self-correspondences of S some of the components are identically-correspondent. For example, in sec. 100 the unit e is always identically-correspondent. Thus constituents may have several rows which are duplicates. If we merely desire to consider those correspondences which the constituent indicates, we may, of course, omit duplicate rows.

116. If one two-row constituent be a part of another, the correspondence indicated by the former may be said to "occur in" that indicated by the latter; as when the latter correspondence occurs the former also occurs.

117. If we regard all collections of units under consideration in an investigation as components of the universal system which comprises all units, or, as is sufficient, as components of the whole system of units considered in the investigation, we may regard every correspondence of undistinguished collections as occurring in one or more self-correspondences of the universal or more limited system. From this point of view we see that a correspondence of two undistinguished collections, or the self-correspondence of a collection, restricts the possible correspondences and self-correspondences of other collections. In some cases it may determine absolutely the correspondences and self-correspondences of the other collections, not permitting

alternative correspondences or self-correspondences, in others it may partially restrict them, in others it may exercise no controlling effect whatever, so that collections may go through all correspondences and self-correspondences with as much freedom as if there were no correspondence already existing.

118. If two collections are such that each can go through all its self-correspondences while the other remains identically-correspondent, they will be said to be *independent*. If two collections are not independent, they will be said to be *related*.

119. If m and m' be the number of self-correspondences of two systems S and S′ respectively, the table representing the joint system S, S′ will have mm' rows if S and S′ are independent.

120. In the self-correspondences of a system every correspondence of undistinguished components occurs; but it is not of course in general the case that in the self-correspondences of any collection all the correspondences of undistinguished components of that collection occur. For example, in sec. 100 the only self-correspondence of a, b, c, is given by the constituent $\begin{smallmatrix} a & b & c \\ c & b & a \end{smallmatrix}$, and here no correspondence of the undistinguished units a, b occurs.

121. When investigating the correspondences of a number of $(n + m)$-ads we may for some time be occupied with the consideration of correspondences in which m of the units always remain identically-correspondent. The absence of change in the correspondence of the m-units may lead us to forget or overlook the fact that we are considering correspondences of the $(m + n)$-ads, and we may suppose that we are dealing with n-ads only. When then we find that a certain correspondence of two n-ads apparently does not exist, we must look closely to see whether we are not really considering correspondences of $(n + m)$-ads, and whether a change in the correspondence of the m units may not lead to the correspondence of the n which is supposed not to exist.

122. Units which in any correspondence of two undistinguished aspects are identically-correspondent may be termed the *foci* of the correspondence. Three or more undistinguished aspects such that the foci of the correspondences are the same in the case of each pair, may be said to be *confocal*. We may also use the term *confocal* as applicable to the case of corresponding components of the corresponding confocal aspects.

123. In cases in which, as mentioned in sec. 121, we consider $(n + m)$-ads as if they were n-ads, we really pass from the consideration of the original units to that of other units which are arrived at by taking the m foci with each of the other units successively, and then regarding the resulting $(m + 1)$-ads as single units.

124. Differences between things can always be ignored, and thus we may at one time regard two collections of units as distinguished, and at another, by ignoring differences between them, as undistinguished. Here we are dealing with certain units, upon which the differences depend, in addition to those of the two collections.

125. For example in the case of the system of fig. 24, although all the graphical units are alike if taken apart from the barbed lines joining them, the two triads

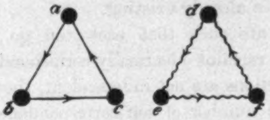


Fig. 24.

a, *b*, *c* and *d*, *e*, *f* are distinguished because plain lines are distinguished from wavy ones. If we ignore the difference between straightness L and waviness W, we are really dealing with the eight units *a*, *b*, *c*, *d*, *e*, *f*, L, W, and instead of dealing with units *a*, *b*, *c*, &c., are really dealing with the triads *a*LW, *b*LW, &c. When we regard the two triads *a*, *b*, *c* and *d*, *e*, *f* as distinguished, we deal with correspondences represented by the constituent consisting of the first, or last, nine rows of the table at the end of the section, in which it will be seen that L and W remain identically-correspondent, and the correspondences are such as would exist if L and W were distinguished. When we ignore the difference between straightness and waviness, we admit correspondences such as $\begin{array}{l} a\,b\,c\,d\,e\,f\,\mathrm{L}\,\mathrm{W} \\ d\,e\,f\,a\,b\,c\,\mathrm{W}\,\mathrm{L} \end{array}$

The table representing the whole system of eight units is as follows :—

a	*b*	*c*	*d*	*e*	*f*	L	W
a	*b*	*c*	*e*	*f*	*d*	L	W
a	*b*	*c*	*f*	*d*	*e*	L	W
b	*c*	*a*	*d*	*e*	*f*	L	W
b	*c*	*a*	*e*	*f*	*d*	L	W
b	*c*	*a*	*f*	*d*	*e*	L	W
c	*a*	*b*	*d*	*e*	*f*	L	W
c	*a*	*b*	*e*	*f*	*d*	L	W
c	*a*	*b*	*f*	*d*	*e*	L	W
d	*e*	*f*	*a*	*b*	*c*	W	L
d	*e*	*f*	*b*	*c*	*a*	W	L
d	*e*	*f*	*c*	*a*	*b*	W	L
e	*f*	*d*	*a*	*b*	*c*	W	L
e	*f*	*d*	*b*	*c*	*a*	W	L
e	*f*	*d*	*c*	*a*	*b*	W	L
f	*d*	*e*	*a*	*b*	*c*	W	L
f	*d*	*e*	*b*	*c*	*a*	W	L
f	*d*	*e*	*c*	*a*	*b*	W	L

126. Many of the relations which collections of units hold to each other are apparently independent of the form of the collections, or of the form of the system S, of which they are components. In dealing with such relations we ignore differences, and regard the units composing the collections as single heaps, *i.e.*, we do not deal with the units $a, b, c, d, \ldots$ of S, but with others $\alpha, \beta, \gamma, \delta, \ldots$ which constitute a single heap, but have the same self-correspondences as $a, b, c, d, \ldots$ have as long as certain other units remain identically-correspondent.

127. Since we can in all cases ignore differences, any system S may be regarded as a single heap, the peculiarities of form which it possesses in any particular investigation being regarded as due to the fact that we are not considering S alone, but in conjunction with other units, those correspondences only of S being dealt with which admit of the additional units remaining identically-correspondent. All statements, therefore, as to the distinguishableness and undistinguishableness of components of S, and as to their being of particular forms may be taken as relative, viz., as statements that the components have the correspondences characteristic of those forms as long as certain units detached from S remain identically-correspondent.

128. It may be laid down generally, that in almost every instance where we seem to investigate a base system S which may be regarded and spoken of as being of n units and of a particular form, we really deal with a single heap system H of n units and a system F which remains identically-correspondent while the units of H go through the correspondences characteristic of the system S.

129. Any collection of units which while another collection C remains identically-correspondent has self-correspondences characteristic of a collection of a special form may be said to be of that form relatively to C.

Sets.

130. If $abcd\ldots$, $pqrs\ldots$, are undistinguished components of a collection $a, b, c, d, \ldots p, q, r, s, \ldots l, m, n, o, \ldots$, then the units $w, x, y, z, \ldots$ which are such that $abcd\ldots lmno\ldots \succ\!\!-\!\!\prec pqrs\ldots wxyz\ldots$ may or may not be units of the collection, and in some cases cannot be selected so as to be units of the collection. If the collection be such that whatever undistinguished components $abcd\ldots$, $pqrs\ldots$ we select, and whatever other component $lmno\ldots$ we select, $w, x, y, z\ldots$ can always be selected from the collection, then the collection will be termed a *set*.

131. A system is obviously a set. A set is not necessarily a system; it may be one of a number of undistinguished sets which together compose a single or multiple system. In most investigations our inquiries are directed towards the discovery of the forms of component sets of the base system. As far as the distribution of its distinguished and undistinguished components is concerned, a set in no way differs from a system.

132. In the self-correspondences of a set every correspondence of its undistinguished

components occurs. Thus the constituent which represents a set has sub-constituents indicating all the correspondences of the components of the set.

133. In a graphical representation of a set the diagram not only indicates what units, &c., are distinguished and what undistinguished, but is such that if we ignore geometrical position in accordance with sec. 41, and the reference letters in accordance with sec. 42, the units, &c., will be actually distinguished and undistinguished, and the diagram will represent the form of the set by being actually of that form.

134. Any collection of units which is not a set may be said to be *imperfect.*

135. If any collection of units is such that its component pairs are all distinguished from the pairs connecting it with units detached from it, the collection is a set. For let $lmn \ldots$ and $pqr \ldots$ be any two undistinguished components of the collection, then if a be any unit of the collection, a unit b which is such that $lmn \ldots a$ is undistinguished from $pqr \ldots b$ must also be a component of the collection, otherwise the pairs connecting b and $p, q, r, \ldots$ will be pairs connecting a unit not of the collection with units of the collection, and they will be undistinguished from the pairs connecting a and $l, m, n, \ldots$ which are all pairs of the collection.

136. Let x be any unit of a single set Q of n units; consider the pairs formed by x with other units of Q; take any one of these xp; let the number of pairs $xp, xq, xr, \ldots$ which are undistinguished from xp, be m; then in the case of any other unit y of Q the number of pairs $yi, yj, yk, \ldots$ which are undistinguished from xp is m also. Further the number of pairs $ax, bx, cx, \ldots$ which are undistinguished from xp is also m; for the number m' of such pairs must be the same in the case of each unit, and thus we have $mn=m'n$, i.e., $m=m'$.

Aspects unique with respect to Collections.

137. If $xyz \ldots abc \ldots >\!\!\!-\!\!\!< uvw \ldots abc \ldots$, then the aspects $xyz \ldots$ and uvw may be said to be *duplicates with respect to* the collection $a, b, c, \ldots$ If there is no duplicate of $xyz \ldots$ with respect to $a, b, c, \ldots$ then $xyz \ldots$ may be said to be *unique with respect to* $a, b, c, \ldots$ It should be observed that if $xyz \ldots$ is unique with respect to $a, b, c, \ldots$ there may be an aspect $uvw \ldots$ such that $xyz \ldots abc \ldots >\!\!\!-\!\!\!< uvw \ldots cab \ldots$

138. If the aspect $abc \ldots$ be unique with respect to the collection $d, e, f, \ldots$ and if the apsect $def \ldots$ be unique with respect to the collection $g, h, i, \ldots$; then $abc \ldots$ is unique with respect to $g, h, i, \ldots$ I give the proof in the case in which the three collections are detached; the proof in other cases is somewhat longer but presents no difficulty. If $abc \ldots$ is not unique with respect to $g, h, i, \ldots$ there are units $p, q, r, \ldots$ such that $abc \ldots ghi >\!\!\!-\!\!\!< pqr \ldots ghi \ldots$, and there are (sec. 94) units $s, t, u, \ldots$ such that $abc \ldots def \ldots ghi \ldots >\!\!\!-\!\!\!< pqr \ldots stu \ldots ghi \ldots$; but $def \ldots$ is unique with respect to $g, h, i, \ldots$ therefore $stu \ldots$ is $def \ldots$, therefore $abc \ldots def$

. . . $\succ\!\!-\!\!\prec$ *pqr* . . . *def* . . . , therefore *abc* . . . is not unique with respect to *d*, *e*, *f*, . . . contrary to the hypothesis; *i.e.*, *abc* . . . is unique with respect to *g*, *h*, *i*, . . .

139. If a single unit *x* be unique with respect to a collection *a*, *b*, *c*, . . . we may represent *x* by the symbol (*abc* . . .) or [*abc* . . .] &c. The two symbols (*abc* . . .) and [*abc* . . .] will, where the different sorts of brackets are distinguished from each other, represent two units which are distinguished from each other, and each unique with respect to *a*, *b*, *c*, . . . ; or we may use the two symbols to represent two undistinguished units *p*, *q* which are each unique with respect to *a*, *b*, *c* . . . , the difference between the brackets indicating that the units *p*, *q* are not identical.

140. If *abc* . . . $\succ\!\!-\!\!\prec$ *pqr* . . . then (*abc* . . .) $\succ\!\!-\!\!\prec$ (*pqr* . . .), where (*abc* . . .) and (*pqr* . . .) may be the same or different units; and (*abc* . . .) *abc* . . . $\succ\!\!-\!\!\prec$ (*pqr* . . .) *pqr* . . . If *abc* . . . $\longleftrightarrow$ *pqr* . . . then (*abc* . . .) and (*pqr* . . .) may or may not be distinguished units.

141. If we consider aspects such as P*abc* . . ., Q*abc* . . ., P*def* . . ., &c., where in each aspect one only of the units P, Q, &c., appears, we may represent P, Q, &c., by brackets of different sorts, and write the units which are unique with respect to P, *a*, *b*, *c*, . . ., &c., thus (*abc* . . .), [*abc* . . .], (*def* . . .), &c., where P is represented by the brackets ( ), Q by the brackets [ ].

142. Suppose $a \equiv (bc)$, $b \equiv (de)$, $e \equiv (fc)$, then we may represent a by the symbol $((de)\,c)$ or $((d\,(fc))\,c)$, each symbol representing a and at the same time an aspect of a collection of which a is a component. We may have such symbols with various different sorts of brackets, *e.g.*, if $d \equiv [mn]$, a will be represented by $(([mn]\,e)\,c)$.

Associates.

143. If *a*, *b*, *c*, . . . be any collection of units, and if λ be another unit, such that the pairs λ*a*, λ*b*, λ*c*, . . . are distinguished from all pairs which λ makes with units which are not components of the collection, λ may be said to be an *associate* of the collection *a*, *b*, *c*, . . .

144. If the pairs λ*a*, λ*b*, λ*c*, . . . are all undistinguished from each other, λ may be termed a *single pair associate.*

145. If some of the pairs are distinguished from each other, λ may be termed a *multiple pair associate.*

146. In the special case in which all the pairs are distinguished from each other a multiple pair associate may be termed a *discrete pair associate.*

147. A single pair associate of a collection can only exist if all the units of the collection are undistinguished from each other. Also in the case of a multiple pair associate of a collection units of the collection which make pairs with the associate which are undistinguished must themselves be undistinguished.

148. An associate of any description may be graphically represented by a graphical unit connected by links with each of the units of which it is an associate.

149. If we desire in the case of a multiple pair associate to indicate the distinguished pairs, we may employ lines of various sorts in lieu of links, thus :—

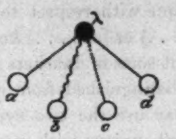


Fig. 25.

150. Many of our conceptions and definitions of systems of units involve the idea of associates, and the graphical definition of systems by means of links is very convenient as enabling this to be visually represented.

151. In many cases units which we might at first sight regard as associates of a system S of some definite form, are really associates of a single heap system H accompanied by a system F which remains self-correspondent while H goes through correspondences characteristic of the form of S (sec. 128).

Unified Aspects.

152. The unit arrived at by regarding any aspect of a collection *a*, *b*, *c*, . . . as a single unit, is unique with respect to the collection and may be represented by the symbol (*abc* . . .).

153. Two aspects when unified are two distinct units, and not one unit. Thus if *abc* . . . and *lmn* . . . are different aspects (*abc* . .) is not (*lmn* . . .).

154. Every aspect is unique with respect to its unified aspect; for if *abc* . . . (*abc* . . .) >—< *lmn* . . . (*abc* . . .), then *abc* . . . >—< *lmn* . . . and then (sec. 140) *abc* . . . (*abc* . . .) >—< *lmn* . . . (*lmn* . . .) ; thus we have *lmn* . . . (*abc* . . .) >—< *lmn* . . . (*lmn* . . .); and (*lmn* . . .) is not (*abc* . . .) (sec. 153), thus (*lmn* . . .) is not unique with respect to *lmn* . . ., which is contrary to sec. 152 ; therefore, &c.

155. If λ and μ be two unified aspects of the same collection they are unique with respect to each other. For, by sec. 152, λ is unique with respect to the collection, and, by sec. 154, the aspect of the collection which is μ when unified is unique with respect to μ, thus, by sec. 138, λ is unique with respect to μ. Similarly μ is unique with respect to λ.

156. The pairs which a unified aspect (*abc* . . .) makes with *a*, *b*, *c*, . . . respectively are all distinguished from each other. For if (*abc* . . .)*a* >—< (*abc* . . .)*b*, then there are units *l*, *m*, . . . such that (*abc* . . .)*abc* . . . >—< (*abc* . . .)*blm* . . ., *i.e.*, such that *abc* . . . >—< *blm* . . . , *i.e.*, such that (*abc* . . .)*abc* . . . >—< (*blm* . . .) *blm* . . . , *i.e.*, such that (*abc* . . .)*blm* . . . >—< (*blm* . . .)*blm*, *i.e.*, such that (*blm* . . .) is not unique with respect to *blm* . . . , contrary to sec. 152, therefore, &c.

157. In the same way it may be shown that the pairs which ($abc\ldots$) makes with a, b, c, . . . respectively are all distinguished from the pairs which ($abc\ldots$) makes with any other units x, y, z, . . . not components of the collection a, b, c, . . .

158. A unified aspect ($abc\ldots$) is accordingly a discrete pair associate of the collection a, b, c, . . . (sec. 146).

159. It should be observed that in the case of a number of undistinguished aspects no unit can be said to be *the* unit arrived at by regarding any particular one of those aspects as unified. All we can say is that any one of a number of units may be so regarded. If, however, one of that number is regarded as representing a particular one of the unified aspects, some other definite unit of the number must be regarded as the unit which represents another given unified aspect, *i.e.*, the two unified aspects will be such that they can only be represented by certain pairs of the units and not by any pair.

160. When we represent aspects by single letters, those letters really represent the unified aspects. Whatever relations as to distinguishableness or undistinguishableness exist between the aspects, there will be precisely the same relations between the unified aspects; so that we may deal with either the unified or non-unified aspects. Thus if A, B, C, D, be the aspects *abcd*, *efgh*, *ijkl*, *uvwx*, when regarded as units, then if $abcdefgh \succ\!\!-\!\!\!-\!\!\prec ijkluvwx$, we have $\mathrm{AB} \succ\!\!-\!\!\!-\!\!\prec \mathrm{CD}$.

161. The conception of a unified aspect is an "accidental" one; for the units representing unified aspects of components of a system S may be regarded as representing any other things holding similar relations to the units of S. The method of defining systems by regarding their units as unified aspects of components of other systems is, however, so convenient and simple that it will be frequently employed, and the accidental part of the definition being borne in mind, no danger can arise from the employment of this method of arriving at systems.

Correspondences of Systems of like Forms.

162. We may consider correspondences of any two independent systems S_1 and S_2 of the same form, in which every component of S_1 corresponds to a component of S_2 of the same form, and we may regard these correspondences as units. The number of such correspondences is in general greater than the number of self-correspondences of each system, as in the case of the latter we only suppose undistinguished components to correspond, and do not admit correspondences of distinguished components of like form.

163. If, however, we start with a correspondence of S_1 and S_2 and then restrict ourselves as regards other correspondences to those in which each component of S_1 corresponds only with such components of S_2 as are undistinguished from that with which it corresponded in the first instance, we shall get the same number of correspondences as there are self-correspondences of each collection S_1, S_2.

164. If we then take another correspondence not included among the former, we shall get a second collection of correspondences equal in number to the former, and so on until the correspondences are all exhausted.

165. For example the six graphical units of the system of fig. 26 constitute two independent systems of the same form. Starting with the correspondence $\frac{abc}{def}$ which we may represent as a unit P, we may add correspondences $\frac{abc}{efd}$ and $\frac{abc}{fde}$ which we may represent by units Q and R respectively. Here we have only correspondences such as those referred to in sec. 163. It is to be observed that we cannot properly say that P represents any particular one of the three correspondences, for they are undistinguished; the three units P, Q, R, together represent the three correspondences; but if P is regarded as representing any definite correspondence Q and R will each represent definite correspondences, for P, Q, R, are each unique with respect to each other. If we now consider the correspondence $\frac{abc}{dfe}$ in which we have components of the same form corresponding as before, we get the correspondences $\frac{abc}{fed}$ and $\frac{abc}{edf}$. We may represent these by the units L, M, N. The whole system of units considered is represented by the following table—

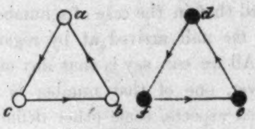


Fig. 26.

a	*b*	*c*	*d*	*e*	*f*	P	Q	R	L	M	N
a	*b*	*c*	*e*	*f*	*d*	Q	R	P	N	L	M
a	*b*	*c*	*f*	*d*	*e*	R	P	Q	M	N	L
b	*c*	*a*	*d*	*e*	*f*	R	P	Q	N	L	M
b	*c*	*a*	*e*	*f*	*d*	P	Q	R	M	N	L
b	*c*	*a*	*f*	*d*	*e*	Q	R	P	L	M	N
c	*a*	*b*	*d*	*e*	*f*	Q	R	P	M	N	L
c	*a*	*b*	*e*	*f*	*d*	R	P	Q	L	M	N
c	*a*	*b*	*f*	*d*	*e*	P	Q	R	N	L	M

166. We may of course consider self-correspondences of a system S in which components of like form correspond which are distinguished from each other. Thus in the case of the system *a*, *b*, *c*, *d*, *e*, of fig. 27 we may consider correspondences such

as $\genfrac{}{}{0pt}{}{abcde}{aedcb}$ or $\genfrac{}{}{0pt}{}{abcde}{acebd}$. It is, however, to be understood that the term "self-correspondence" will always be used, as heretofore, with reference to self-correspondences which involve the correspondence of undistinguished collections only.

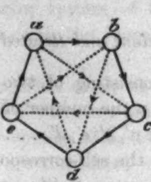


Fig. 27.

167. The two systems S and X of sec. 81 are of the same form. In the tabular representation of either the unified columns will represent the units of the other. Further, S and X are independent systems, no special relation except that of similarity of form exists between them. Each aspect of S is arrived at by considering a correspondence of S and X; it may in fact be regarded as such a correspondence, so that a unified aspect is a unified correspondence, and the whole system of unified aspects of S represent a system of unified correspondences of two systems of the same form, in which we are restricted to such correspondences as those referred to in sec. 163.

168. When two systems are regarded as corresponding they may be spoken of as being *projections* of each other in as many ways as there are unified correspondences.

169. If we represent the units of one of two independent systems of the same form by the symbols (λa), (λb), (λc), &c., we may represent those of the other by the symbols (μa), (μb), (μc), &c., where in one correspondence we may conveniently suppose that (λa) corresponds to (μa), (λb) to (μb), and so on; but it is not to be supposed that this correspondence is distinguished from others.

Replicas.

170. If $a, b, c, d, \ldots$ and $\alpha, \beta, \gamma, \delta, \ldots$ be two systems of units such that a and α are unique with respect to each other, as also b and β, c and γ, &c., and if, a and b being any two units of the first system, when $a \succ\!\!-\!\!\prec b$ we have also $a\alpha \succ\!\!-\!\!\prec b\beta$, then $\alpha, \beta, \gamma, \delta, \ldots$ may be called a *replica* of $a, b, c, d, \ldots$

171. The replica of a system S is of the same form as S, and has the same relations to other systems as S has. In the tabular representation of S and its replica, whatever transpositions of the letters representing an aspect of S takes place in passing from one row to another, precisely the same transposition takes place in the case of the letters representing an aspect of the replica.

172. The replica of a multiple system S may have some single systems in common with S; some of the single systems may be their own replicas.

173. The letters placed adjacent to graphical units for the purpose of reference compose a system which is a replica of the graphical system.

Independent and Related Systems.

174. Let S, S′ be a system consisting of two detached systems S and S′; let $a, b, c, d, \ldots$ be the units of S, n the number of those units, and m the number of the self-correspondences of S. Let $a', b', c', d', \ldots$ be the units of S′, n' the number of those units, and m' the number of the self-correspondences of S′. Let μ be the number of self-correspondences of the system S, S′: μ cannot be $> mm'$, otherwise there would be duplicate rows in the tabular representation of S, S′. Consider now a set of rows in the tabular representation of S, S′ obtained by taking any row R and all others in which the letters $a', b', c', d', \ldots$ remain untransposed from the order they have in R. Let the number of rows in the set be k. A transposition indicated by two rows of the set if made to operate on any row of the set will clearly give a row also of the set. Now take any fresh row not of the set; this must also be one of a set of k rows detached from the former set. Thus all the rows divide up into m' sets of k rows, and we have $m'k=\mu$. If k' be the corresponding number in the case where $a, b, c, d, \ldots$ remain untransposed, we have $mk'=\mu$. Thus we have $m'k=mk'=\mu=mm'$ or $< mm'$.

175. Let $\mu=mm'$, then $k=m$, $k'=m'$, and the two systems are independent.

176. We must have $mm'=\mu$ unless m and m' have a common integral factor; so that two systems S and S′ must be independent unless the numbers of their respective self-correspondences have a common factor. The two systems may of course be independent when m and m' have a common factor.

177. If m and m' are prime to each other S and S′ may be said to be *prime* to each other; so that systems which are prime to each other are independent.

178. If $mm' < \mu$, m and m' must have a common factor, and the two systems S and S′ will be *related*. If $l'm'n' \ldots$, $x'y'z' \ldots$ are undistinguished components of S′, and $abcd \ldots$ be an aspect of the whole system S, then the aspects $l'm'n' \ldots abcd \ldots$ and $x'y'z' \ldots abcd \ldots$ will not in general be undistinguished from each other; and any graphical diagram representing the system S, S′ must have lines, or successions of lines, connecting units of S to units of S′, so that S and S′ cannot be drawn on separate sheets of paper.

179. If we have three detached systems, S_1, S_2, S_3; and S_1 and S_2 are related, and also S_1 and S_3, it does not follow that S_2 and S_3 are related; the single consideration that m_1 and m_2 may have a common factor, and also m_1 and m_3, without m_2 and m_3 having one, shows this.

180. If $m = m' = \mu$, then S and S′ are replicas of each other.

181. If $m = \mu$, and $m \neq m'$, m' will be a factor of m, and S′ may be said to be a *factor system* of S. We have here $m = m'k = \mu$.

182. If S′ be a factor system of S we have $k' = 1$; *i.e.*, there is no self-correspondence of S, S′, other than the identical-correspondence, in which S is identically-correspondent. If S′ is not a factor system of S, we have $k > 1$, and there are self-correspondences of S, S′, other than the identical-correspondence, in which S is identically-correspondent.

183. Hence if S′ be a factor system of S, there are no units of S′ which are duplicates with respect to S. And if there are units of S′ which are duplicates with respect to S, then S′ is not a factor system of S. Further, if S′ be not a factor system of S, there are units of S′ which are duplicates with respect to S, unless S and S′ are replicas of each other. And if there are no units of S′ which are duplicates with respect to S, then S′ is a factor system of S, unless S and S′ are replicas of each other.

184. If S′ be a factor system of S, each single system of S′ must be so also. For if m_1' be the number of self-correspondences of S_1' a single system of S′, we have $m_1' \ngtr m'$, *i.e.*, $m_1'm \ngtr mm' < \mu$, *i.e.*, $m_1'm < \mu$.

185. If S′ be a factor system of S, it is also a factor system of Δ, the single system composed of the unified aspects of S. This follows immediately from the fact that the combined system S, Δ has the same number of self-correspondences as S has.

186. Hence also every single system of S′, a factor system of S, must be a factor system of Δ.

187. A system which has no factor systems, except systems of one unit, may be termed a *prime system*.

188. If S″ is a factor system of S′, and S′ is a factor system of S, then S″ is a factor system of S. For let a'', b'' units of S″ be duplicates with respect to S; then we have $a''\mathrm{S} \succ\!\!-\!\!\!-\!\!\prec b''\mathrm{S}$. Now if c' be any unit of S′, there must be a unit d' such that $a''c'\mathrm{S} \succ\!\!-\!\!\!-\!\!\prec b''d'\mathrm{S}$; and since S′ is a factor of S, we cannot have $c'\mathrm{S} \succ\!\!-\!\!\!-\!\!\prec d'\mathrm{S}$, unless c' is d'. Thus we have $a''c'\mathrm{S} \succ\!\!-\!\!\!-\!\!\prec b''c'\mathrm{S}$, *i.e.*, we have $a''c' \succ\!\!-\!\!\!-\!\!\prec b''c'$, whatever unit c' of S we take, *i.e.*, a'' is b'', and there are no units of S″ duplicates with respect to S, *i.e.*, S″ is a factor system of S.

Three Modes of Compounding Systems.

189. There are three modes of deriving a system from two or more other systems to which a passing reference may here be made. In the first the compound system is arrived at by regarding the n-ads connecting n independent or related systems as units.

190. Again, we may have a system which may be regarded as composed of n independent (and therefore detached) undistinguished sets, each of a given form F, and such that their unified aspects compose a system of the form F′.

191. An important special case of such a compound system is that in which the form

F is that of a single heap H of m units. Here F' being the form of any system S, the compound system S_m differs from S in that we have in lieu of any unit a of S a single heap of m units, each unit of which may be called a, the form relations between the connecting r-ads of r of the heaps being the same as those existing between the r-ads of S. Thus if in S we have $abcd \succ\!\!-\!\!\!-\!\!\prec pqrs$, in S_m we shall also have $abcd \succ\!\!-\!\!\!-\!\!\prec pqrs$, whatever units of the heaps $aaa \ldots$, $bbb \ldots$, &c., we select.

192. If we combine two connected component collections L and M of S, the resulting collection cannot contain those units which are common to L and M twice over; *i.e.*, the result of combining the collections a, b, c, d, and c, d, e, f is the collection a, b, c, d, e, f. If in S_m we select collections a, b, c, d and c, d, e, f so that the units c, d of the first are not the same units as c, d of the second, the sum of the two collections will be the collection a, b, c, c, d, d, e, f.

193. The third mode of composition is that in which the derived system has all the self-correspondences which each of a number of systems, of the same number of units, has. We may represent the units of such a system by symbols

$$(\mathrm{A}a \ldots), (\mathrm{B}b \ldots), (\mathrm{C}c \ldots), \&c.,$$

where A, B, C . . . are units of one of the compounded systems, a, b, c those of another, and so on.

General Method of Graphically Representing a System.

194. Let each unit of a system S, each unified column, each unified row, and each element of its tabular representation, be represented by a graphical unit, using different kinds of graphical units in the case of the units of S, the rows, columns, and elements respectively, four kinds in all. Connect each graphical unit which represents an element by links to

(1.) the graphical unit representing the unit of S of which the element represents a unit aspect;

(2.) the graphical unit representing the unified row in which the element lies;

(3.) the graphical unit representing the unified column in which the element lies.

We get a graphical representation of a system of $2n+m+mn$ units, of which S is a component system.

195. It is obviously not always necessary to employ the somewhat cumbrous mode of graphical representation here given; simpler methods can be adopted in special cases. Frequently, as we have already seen, it will not be necessary to have any auxiliary graphical units, but merely those representing the units of S itself.

Networks.

196. The pairs of any single collection of pairs are either all component pairs of a single system of units, or all connecting pairs of two single systems of units.

197. Where a single system P of pairs connects two single systems S and Σ, the number of pairs of P which connect any unit a of S to units of Σ is the same as the number of pairs of P which connect any other unit b of S to units of Σ. The number in the case of units of S is the same as the corresponding number in the case of units of Σ if S and Σ contain the same number of units, but not otherwise.

198. Where the pairs of a single system of pairs are components of a single system S of units, the number μ of pairs of the former system which connect any unit a of S to other units of S is the same as that in the case of any other unit b of S. Also the number of such pairs connecting units of S to a is the same as that of those connecting units of S to any other unit b of S, being in both cases also μ (sec. 136).

199. A single system of component pairs of any single system of units constitutes a *simple network* of which the number μ of the last section may be called the *way-number.* This network consists of one or more portions each continuous and detached from the other portions. Where there are two or more detached continuous portions of a simple network, each is undistinguished from the others, for component pairs of distinguished portions would be distinguished.

200. Every simple network is accompanied by one in which the pairs connect the same units but in the reverse order, so that if ab is a pair of one network, ba is a pair of the other. The two networks may be called the *reverses* of each other. If we represent the unified pairs of the one by single letters α, α, α, α, we may represent those of the other by α', α', α', α'. Here the sorts of the letters may be regarded as representing the networks when regarded as units.

201. We may use the symbol (α) to represent the network, of which α is a unified pair. Here (α) takes the place of the sort of α. Or we may use (ab) (sec. 263).

202. The units of a continuous detached portion of a simple network form a set, for any two are connected by a chain of one or more pairs of the network, while no component unit is connected by such a chain with a detached unit, so that all component pairs are distinguished from all connecting pairs of the collection (sec. 135).

203. Thus a simple network divides the units of a single system into one or more detached sets, each of the same number of units. If, then, ρ be the number of units in each set, and σ the number of sets, $\rho\sigma=n$ the number of units in the system. Thus ρ and σ must each be integral factors of n.

204. Equations such as

$$(\mathrm{S})=\frac{p}{a}\cdot\frac{q}{b}\cdot\frac{r}{c}\cdot\frac{s}{d},$$

where $pa=qb=rc=sd=n$, may be employed to denote the fact that there is a simple network which divides the units of S into p sets of a units, another which divides them into q sets of b units, and so on. We may have equations such as

$$(\mathrm{S})=\frac{p}{a}\cdot\frac{p}{a}\cdot\frac{p}{a}\cdot\frac{q}{b}\cdot\frac{q}{b},$$

showing that there are three different simple networks which divide S into p sets of a units, and so on. We may in such a case write the equation thus :—

$$(\mathrm{S})=\left(\frac{p}{a}\right)^3\cdot\left(\frac{q}{b}\right)^2$$

205. Two distinguished simple networks, components of a single system S, either divide S into the same detached sets, or the pairs of one of the simple networks are pairs connecting the detached continuous portions of the other. For pairs belonging to one simple network must either be all component pairs of the sets into which S is divided by the other simple network or all pairs connecting them.

206. A network composed of two or more simple networks may be called a *compound* network, and may be called *double, treble,* &c., according to the number of the component simple networks. A compound network will consist of one or more undistinguished detached continuous compound portions. The units of each of these portions constitute a set.

207. Where a network simple or compound consists of only one detached portion, it may be said to be *complete*.

208. If the pairs of each simple network of a compound network N connect detached portions of the compound network composed of the remaining simple networks of N, then the compound network N may be said to be *pure*.

209. Any two simple networks of a pure compound network may be said to be *outside* each other.

210. If each pair of a simple network connects units which are both components of the same detached portion of a simple or compound network, the latter network may be said to *enclose* the former.

Chains.

211. A succession of undistinguished pairs, *ab, bc, cd* . . . may be termed a *simple chain*. Where the chain has no terminal units it may be said to be *closed*. Every simple chain is a portion of a closed chain, unless it contains one pair only, when it may be a pair connecting two systems.

212. *Compound chains* are such as contain distinguished pairs, or undistinguished pairs of opposite polarities.

213. In the case of the pairs connecting two systems we may have networks consisting entirely of undistinguished pairs ; but every chain in each consists of successions of pairs alternately of opposite polarities.

214. A complete network of a system contains simple or compound chains connecting every two units of the system.

215. If a chain of pairs of a pure compound network contains one pair only from one of the component simple networks, it cannot be closed, for if it were the single

pair would not connect two detached portions of the compound network composed of the simple networks from which the remaining pairs are taken, but two units of a continuous portion.

216. The number of pairs in a closed chain may be termed its *period*. The period of a closed chain is of course the same as the number of units it connects.

217. A symmetrical pair of units may be regarded as constituting a simple closed chain of period 2; thus

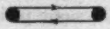


Fig. 28.

218. It may also be convenient in some cases to regard each unit as connected to itself by a single barbed line constituting a simple closed chain of period 1, thus

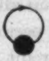


Fig. 29.

219. We may represent a chain of pairs thus $a\lambda b\mu c\nu d\rho e$, where a, b, c, d, e represent units, and the sorts of λ, μ, ν, ρ the networks of which the pairs ab, bc, cd, de, are respectively components; λ, μ, ν, &c., being the letters placed alongside of the plain lines if we employ the graphical method of sec. 64. In some cases it will not be necessary to employ specific letters to represent the units, they may be represented by the spaces between the letters representing the unified pairs, *e.g.*, we may represent the chain given above thus $a\lambda\mu\nu\rho e$, where only the terminal units are given. If we have $a\lambda\mu\nu\rho e$ and $a\pi\sigma e$, we see that the two units a, e are connected by the two different chains $\lambda\mu\nu\rho$ and $\pi\sigma$.

220. We may have equations such as

$$\lambda\mu\nu\rho=\pi\sigma=\kappa,$$

denoting the fact that the three chains $\lambda\mu\nu\rho$, $\pi\sigma$, κ can have the same terminals, and we may write a chain such as $\lambda\mu\mu\mu\nu$ for shortness $\lambda\mu^3\nu$, and similarly in other cases.

221. We may employ as the symbol to be attached to the barbed line of sec. 218 in accordance with the method of sec. 64 the symbol 1. An equation such as $\lambda\mu\nu=1$ will then show that the chain $\lambda\mu\nu$ on the left hand side of the equation is closed.

Groups—Circuits.

222. Any single set which is such that each component unit is unique with respect to each of the others, may be termed a *group*.

223. The single system Δ of unified aspects of any system (sec. 185) is a group, as each unified aspect is unique with respect to each of the others.

224. Every component set of a group is a group.

225. The table, or constituent of a table, representing a group of n units has n rows, a letter of any one sort appearing once and once only in each column.

226. The simple networks of a group are all one-way (sec. 199) networks. The closed chains which constitute the detached portions of any network of a group may be called *simple circuits.* Any closed compound chain of a group may be called a *compound circuit.*

227. If the component pairs of one simple circuit are undistinguished from those of another, the two circuits must have the same period.

228. If the period of a simple circuit be rs where r and s are integers, there will be r simple circuits of period s, and s of period r, connecting the units of the circuit.

229. Now the number of units in a simple circuit of a group of n units must be a factor of n (sec. 203); so that if n be a prime number, there is only one form of group; for one simple circuit must contain all the units, and this being given all the other circuits are given; they are all of period n.

230. In a group if the pairs of one circuit are distinguished from those of another, but both circuits are of the same period, they may be said to be *similar.* The pairs of such circuits may also be said to be similar.

231. If $a, b, c, d, e, \ldots.,$ A, B, C, D, E, ... be units of a group, and if $a, b, c, d, e, \ldots$ constitute a simple circuit in the order given, and if the pairs aA, bB, cC, dD, ... be all undistinguished from each other, then the units A, B, C, D, E, ... constitute a similar circuit in the order given.

232. In the case of a group the terminals of any chain $\lambda\mu\nu\rho$ constitute a pair of a definite simple network (α), *i.e.*, we cannot have $\lambda\mu\nu\rho=\alpha$, and $\lambda\mu\nu\rho=\beta$.

233. We may use the symbol $(\alpha\beta\gamma)$ to represent the network (λ) where $\lambda=\alpha\beta\gamma$.

234. The network of which the two terminals of a chain of pairs are a component pair, may be termed the *product* of the networks of which the pairs composing the chain are components; the order of the networks in the product being of course the same as the order of their component pairs in the chain.

235. A pure complete network furnishes chains connecting every pair of units of a group, and thus if $\alpha, \beta, \gamma, \delta, \ldots$ be unified pairs of the simple networks of such a network, we can with them make chains $\alpha\beta$, $\beta\gamma^2$, $\delta\alpha$, &c., whose terminals constitute pairs of every simple network of the group. A group is accordingly fully defined if one of its pure complete networks is given.

236. We have, whatever pair α may be, $\alpha\alpha'=1$ (sec. 200), and if α be a symmetrical pair $\alpha=\alpha'$, and thus $\alpha^2=1$.

237. If $\alpha\beta=\beta\alpha$, the two networks (α) and (β) may be said to be *commutative.*

238. If a simple network is commutative with each of a number of others, it is commutative with every simple network which is enclosed in the compound network composed of the latter.

239. The system S arrived at by compounding together a number of independent groups in the mode described in sec. 189 is a group having component sets of the form

of each of the original groups. We may fully define the group S by a pure complete network composed of a number of pure networks such that each detached portion of one is composed of units constituting a group of the form of one of the original groups.

Groups containing from one to twelve Units.

240. In the following twelve sections I shall denote the number of units in a group by n; f will denote the number of forms of groups for any value of n; G the graphical representation; T the tabular; and (S) will be the symbol described in section 204. Where f is greater than unity, the symbols G, T, and (S) will have numerical suffixes corresponding to the different forms. In the graphical representation, only such lines will be drawn as are necessary to completely define the group, and in some cases alternative representations will be given, obtained by taking different circuits. The values of n taken are from 1 to 12 inclusive.

241. If $n=1$ we have $f=1$,

$(S)=\frac{1}{1}$, G= , T=a.

Fig. 30.

242. If $n=2$ we have $f=1$,

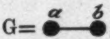
$(S)=\frac{1}{2}$, G= , T=

Fig. 31.

$$\begin{array}{cc} a & b \\ b & a. \end{array}$$

243. If $n=3$ we have $f=1$,

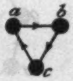
$(S)=\frac{1}{3}$, G= , T=

Fig. 32.

$$\begin{array}{ccc} a & b & c \\ b & c & a \\ c & a & b. \end{array}$$

244. If $n=4$ we have $f=2$,

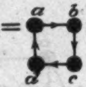
$(S)_1=\frac{1}{4}\frac{2}{2}$, G_1= , T_1=

Fig. 33.

$$\begin{array}{cccc} a & b & c & d \\ b & c & d & a \\ c & d & a & b \\ d & a & b & c. \end{array}$$

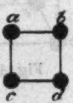
$(S)_2=\left(\frac{2}{2}\right)^3$, G_2= , T_2=

Fig. 34.

$$\begin{array}{cccc} a & b & c & d \\ b & a & d & c \\ c & d & a & b \\ d & c & b & a. \end{array}$$

245. If $n=5$ we have $f=1$,

$(S)=\left(\frac{1}{5}\right)^3$, G=

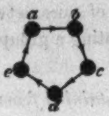


Fig. 35.

$$,\ T=\begin{array}{ccccc} a & b & c & d & e \\ b & c & d & e & a \\ c & d & e & a & b \\ d & e & a & b & c \\ e & a & b & c & d. \end{array}$$

246. If $n=6$ we have $f=2$,

$(S)_1=\frac{1}{6}\cdot\frac{2}{3}\cdot\frac{3}{2}$, $G_1=$

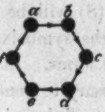


Fig. 36.

or

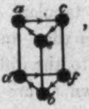


Fig. 37.

$$,\ T_1=\begin{array}{cccccc} a & b & c & d & e & f \\ b & c & d & e & f & a \\ c & d & e & f & a & b \\ d & e & f & a & b & c \\ e & f & a & b & c & d \\ f & a & b & c & d & e. \end{array}$$

$(S)_2=\frac{2}{3}\cdot\left(\frac{3}{2}\right)^3$, $G_2=$

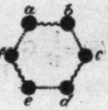


Fig. 38.

or

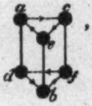


Fig. 39.

$$,\ T_2=\begin{array}{cccccc} a & b & c & d & e & f \\ b & a & f & e & d & c \\ c & d & e & f & a & b \\ d & c & b & a & f & e \\ e & f & a & b & c & d \\ f & e & d & c & b & a. \end{array}$$

247. If $n=7$ we have $f=1$,

$(S)=\left(\frac{1}{7}\right)^3$, G=

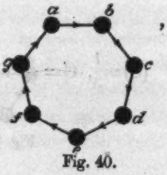


Fig. 40.

$$,\ T=\begin{array}{ccccccc} a & b & c & d & e & f & g \\ b & c & d & e & f & g & a \\ c & d & e & f & g & a & b \\ d & e & f & g & a & b & c \\ e & f & g & a & b & c & d \\ f & g & a & b & c & d & e \\ g & a & b & c & d & e & f. \end{array}$$

248. If $n=8$ we have $f=5$,

$(S)_1=\left(\frac{4}{2}\right)^7$, $G_1=$

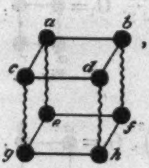


Fig. 41.

$$,\ T_1=\begin{array}{cccccccc} a & b & c & d & e & f & g & h \\ b & a & d & c & f & e & h & g \\ c & d & a & b & g & h & e & f \\ d & c & b & a & h & g & f & e \\ e & f & g & h & a & b & c & d \\ f & e & h & g & b & a & d & c \\ g & h & e & f & c & d & a & b \\ h & g & f & e & d & c & b & a. \end{array}$$

$(S)_2=\left(\frac{4}{2}\right)^3\cdot\frac{2}{4}$, $G_2=$

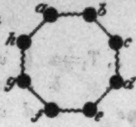


Fig. 42.

or

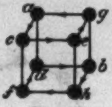


Fig. 43.

$$, T_2=\begin{array}{cccccccc}a&b&c&d&e&f&g&h\\ b&a&h&g&f&e&d&c\\ c&d&e&f&g&h&a&b\\ d&c&b&a&h&g&f&e\\ e&f&g&h&a&b&c&d\\ f&e&d&c&b&a&h&g\\ g&h&d&b&c&d&e&f\\ h&g&f&e&d&c&b&a.\end{array}$$

$(S)_3=\left(\frac{1}{8}\right)^2\frac{2}{4}\cdot\frac{4}{2}$, $G_3=$

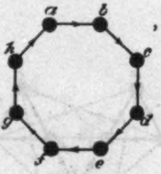


Fig. 44.

$$, T_3=\begin{array}{cccccccc}a&b&c&d&e&f&g&h\\ b&c&d&e&f&g&h&a\\ c&d&e&f&g&h&a&b\\ d&e&f&g&h&a&b&c\\ e&f&g&h&a&b&c&d\\ f&g&h&a&b&c&d&e\\ g&h&a&b&c&d&e&f\\ h&a&b&c&d&e&f&g.\end{array}$$

6

$(S)_4=\left(\frac{2}{4}\right)^2\cdot\left(\frac{4}{2}\right)^3$, $G_4=$

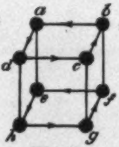


Fig. 45.

$$, T_4=\begin{array}{cccccccc}a&b&c&d&e&f&g&h\\ b&c&d&a&f&g&h&e\\ c&d&a&b&g&h&e&f\\ d&a&b&c&h&e&f&g\\ e&f&g&h&a&b&c&d\\ f&g&h&e&b&c&d&a\\ g&h&e&f&c&d&a&b\\ h&e&f&g&d&a&b&c.\end{array}$$

$(S)_5=\left(\frac{2}{4}\right)^3\cdot\frac{4}{2}$, $G_5=$

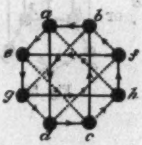


Fig. 46.

$$, T_5=\begin{array}{cccccccc}a&b&c&d&e&f&g&h\\ b&c&d&a&h&e&f&g\\ c&d&a&b&g&h&e&f\\ d&a&b&c&f&g&h&e\\ e&f&g&h&a&b&c&d\\ h&e&f&g&b&c&d&a\\ g&h&e&f&c&d&a&b\\ f&g&h&e&d&a&b&c.\end{array}$$

249. If $n=9$ we have $f=2$,

$$(S)_1=\left(\frac{1}{9}\right)^3\cdot\frac{3}{3},\ G_1=$$

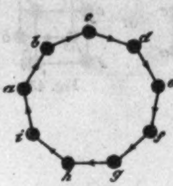


Fig. 47.

$$,\ T_1=\begin{array}{ccccccccc} a & b & c & d & e & f & g & h & i \\ b & c & d & e & f & g & h & i & a \\ c & d & e & f & g & h & i & a & b \\ d & e & f & g & h & i & a & b & c \\ e & f & g & h & i & a & b & c & d \\ f & g & h & i & a & b & c & d & e \\ g & h & i & a & b & c & d & e & f \\ h & i & a & b & c & d & e & f & g \\ i & a & b & c & d & e & f & g & h. \end{array}$$

$$(S)_2=\left(\frac{3}{3}\right)^4,\ G_2=$$

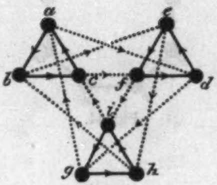


Fig. 48.

$$,\ T_2=\begin{array}{ccccccccc} a & b & c & d & e & f & g & h & i \\ b & c & a & e & f & d & h & i & g \\ c & a & b & f & d & e & i & g & h \\ d & e & f & g & h & i & a & b & c \\ e & f & d & h & i & g & b & c & a \\ f & d & e & i & g & h & c & a & b \\ g & h & i & a & b & c & d & e & f \\ h & i & g & b & c & a & e & f & d \\ i & g & h & c & a & b & f & d & e. \end{array}$$

250. If $n=10$ we have $f=2$,

$$(S)_1=\left(\frac{1}{10}\right)^2\cdot\left(\frac{2}{5}\right)^2\cdot\frac{5}{2},\ G_1=$$

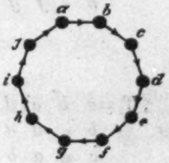


Fig. 49.

or

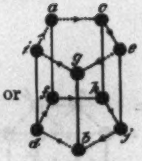


Fig. 50.

$$,\ T_1=\begin{array}{cccccccccc} a & b & c & d & e & f & g & h & i & j \\ b & c & d & e & f & g & h & i & j & a \\ c & d & e & f & g & h & i & j & a & b \\ d & e & f & g & h & i & j & a & b & c \\ e & f & g & h & i & j & a & b & c & d \\ f & g & h & i & j & a & b & c & d & e \\ g & h & i & j & a & b & c & d & e & f \\ h & i & j & a & b & c & d & e & f & g \\ i & j & a & b & c & d & e & f & g & h \\ j & a & b & c & d & e & f & g & h & i. \end{array}$$

$$(\mathrm{S})_2=\left(\frac{2}{5}\right)^2\cdot\left(\frac{5}{2}\right)^5,\ \mathrm{G}_2=$$

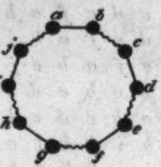


Fig. 51.

or

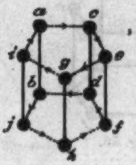


Fig. 52.

$$,\ \mathrm{T}_2=\begin{array}{cccccccccc}
a & b & c & d & e & f & g & h & i & j \\
b & a & j & i & h & g & f & e & d & c \\
c & d & e & f & g & h & i & j & a & b \\
d & c & b & a & j & i & h & g & f & e \\
e & f & g & h & i & j & a & b & c & d \\
f & e & d & c & b & a & j & i & h & g \\
g & h & i & j & a & b & c & d & e & f \\
h & g & f & e & d & c & b & a & j & i \\
i & j & a & b & c & d & e & f & g & h \\
j & i & h & g & f & e & d & c & b & a.
\end{array}$$

251. If $n=11$ we have $f=1$,

$$(\mathrm{S})=\left(\frac{1}{11}\right)^5,\ \mathrm{G}=$$

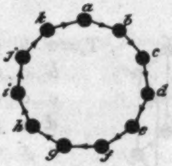


Fig. 53.

$$,\ \mathrm{T}=\begin{array}{ccccccccccc}
a & b & c & d & e & f & g & h & i & j & k \\
b & c & d & e & f & g & h & i & j & k & a \\
c & d & e & f & g & h & i & j & k & a & b \\
d & e & f & g & h & i & j & k & a & b & c \\
e & f & g & h & i & j & k & a & b & c & d \\
f & g & h & i & j & k & a & b & c & d & e \\
g & h & i & j & k & a & b & c & d & e & f \\
h & i & j & k & a & b & c & d & e & f & g \\
i & j & k & a & b & c & d & e & f & g & h \\
j & k & a & b & c & d & e & f & g & h & i \\
k & a & b & c & d & e & f & g & h & i & j.
\end{array}$$

252. If $n=12$ we have $f=5$,

$$(\mathrm{S})_1=\left(\frac{1}{12}\right)^2\frac{2}{6}\cdot\frac{3}{4}\cdot\frac{4}{3}\cdot\frac{6}{2},\ \mathrm{G}_1=$$

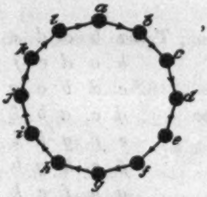


Fig. 54.

$$,\ \mathrm{T}_1=\begin{array}{cccccccccccc}
a & b & c & d & e & f & g & h & i & j & k & l \\
b & c & d & e & f & g & h & i & j & k & l & a \\
c & d & e & f & g & h & i & j & k & l & a & b \\
d & e & f & g & h & i & j & k & l & a & b & c \\
e & f & g & h & i & j & k & l & a & b & c & d \\
f & g & h & i & j & k & l & a & b & c & d & e \\
g & h & i & j & k & l & a & b & c & d & e & f \\
h & i & j & k & l & a & b & c & d & e & f & g \\
i & j & k & l & a & b & c & d & e & f & g & h \\
j & k & l & a & b & c & d & e & f & g & h & i \\
k & l & a & b & c & d & e & f & g & h & i & j \\
l & a & b & c & d & e & f & g & h & i & j & k
\end{array}$$

$$(\mathrm{S})_2=\left(\frac{2}{6}\right)^3\cdot\frac{4}{3}\cdot\left(\frac{6}{2}\right)^3,\ \mathrm{G}_2=$$

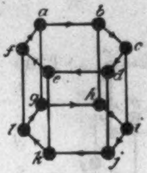


Fig. 55.

$$,\ \mathrm{T}_2=\begin{array}{cccccccccccc}
a & b & c & d & e & f & g & h & i & j & k & l \\
b & c & d & e & f & a & h & i & j & k & l & g \\
c & d & e & f & a & b & i & j & k & l & g & h \\
d & e & f & a & b & c & j & k & l & g & h & i \\
e & f & a & b & c & d & k & l & g & h & i & j \\
f & a & b & c & d & e & l & g & h & i & j & k \\
g & h & i & j & k & l & a & b & c & d & e & f \\
h & i & j & k & l & g & b & c & d & e & f & a \\
i & j & k & l & g & h & c & d & e & f & a & b \\
j & k & l & g & h & i & d & e & f & a & b & c \\
k & l & g & h & i & j & e & f & a & b & c & d \\
l & g & h & i & j & k & f & a & b & c & d & e.
\end{array}$$

$$(\mathrm{S})_3=\frac{2}{6}\cdot\frac{4}{3}\cdot\left(\frac{6}{2}\right)^7,\ \mathrm{G}_3=$$

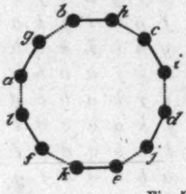


Fig. 56.

or

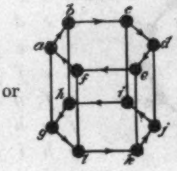


Fig. 57.

$$,\ \mathrm{T}_3=\begin{array}{cccccccccccc}
a & b & c & d & e & f & g & h & i & j & k & l \\
b & c & d & e & f & a & h & i & j & k & l & g \\
c & d & e & f & a & b & i & j & k & l & g & h \\
d & e & f & a & b & c & j & k & l & g & h & i \\
e & f & a & b & c & d & k & l & g & h & i & j \\
f & a & b & c & d & e & l & g & h & i & j & k \\
g & l & k & j & i & h & a & f & e & d & c & b \\
h & g & l & k & j & i & b & a & f & e & d & c \\
i & h & g & l & k & j & c & b & a & f & e & d \\
j & i & h & g & l & k & d & c & b & a & f & e \\
k & j & i & h & g & l & e & d & c & b & a & f \\
l & k & j & i & h & g & f & e & d & c & b & a.
\end{array}$$

$$(\mathrm{S})_4=\left(\frac{3}{4}\right)^3\cdot\frac{4}{3}\cdot\left(\frac{6}{2}\right)^3,\ \mathrm{G}_4=$$

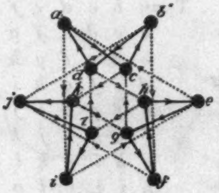


Fig. 58.

$$,\ \mathrm{T}_4=\begin{array}{cccccccccccc}
a & b & c & d & e & f & g & h & i & j & k & l \\
b & a & d & c & j & i & l & k & f & e & h & g \\
c & d & b & a & g & h & f & e & k & l & j & i \\
d & c & a & b & l & k & i & j & h & g & e & f \\
e & f & g & h & i & j & k & l & a & b & c & d \\
f & e & h & g & b & a & d & c & j & i & l & k \\
g & h & f & e & k & l & j & i & c & d & b & a \\
h & g & e & f & d & c & a & b & l & k & i & j \\
i & j & k & l & a & b & c & d & e & f & g & h \\
j & i & l & k & f & e & h & g & b & a & d & c \\
k & l & j & i & c & d & b & a & g & h & f & e \\
l & k & i & j & h & g & e & f & d & c & a & b.
\end{array}$$

$(\mathrm{S})_5=\left(\frac{4}{3}\right)^4\cdot\left(\frac{6}{2}\right)^3$, $\mathrm{G}_5=$

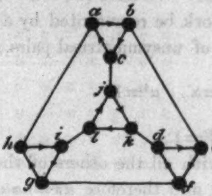


Fig. 59.

$$, \mathrm{T}_5= \begin{array}{cccccccccccc}
a & b & c & d & e & f & g & h & i & j & k & l \\
b & c & a & l & j & k & d & e & f & h & i & g \\
c & a & b & g & h & i & l & j & k & e & f & d \\
d & e & f & a & b & c & j & k & l & g & h & i \\
e & f & d & i & g & h & a & b & c & k & l & j \\
f & d & e & j & k & l & i & g & h & b & c & a \\
g & h & i & c & a & b & e & f & d & l & j & k \\
h & i & g & k & l & j & c & a & b & f & d & e \\
i & g & h & e & f & d & k & l & j & a & b & c \\
j & k & l & f & d & e & b & c & a & i & g & h \\
k & l & j & h & i & g & f & d & e & c & a & b \\
l & j & k & b & c & a & h & i & g & d & e & f.
\end{array}$$

Some General Forms of Groups.

253. The graphical representations of the preceding forms suggest others which exist in the case of larger numbers of units. Thus the form in which a simple circuit passes through all the units of the group appears for all the given values of n; it obviously also exists as one form of group for every other value of n.

254. So if n be even, a form such as that given by the first figure of G_2 when $n=4$, 6, 8, and 10, and by the first figure of G_3 when $n=12$, in which all the units are connected by a continuous chain of non-polar lines of two kinds, clearly exists whatever value n has.

255. If $n=2^m$ we have the form such as G when $n=2$
G_2 ,, 4
G_1 ,, 8

in which all pairs are symmetrical. This form is closely related to the important one considered in Logic (sec. 381), which may be derived from it by ignoring the differences between pairs constituting a pure complete network.

*A Family of Groups.**

256. Let us consider groups in which every circuit is of period 2 or 4. Some of the symmetrical pairs of these groups are component pairs of sets of four units composing simple circuits of period 4, say are *diagonal pairs* (ae in fig. 43 is a diagonal pair); while some (*e.g.*, cf in fig. 43) are not diagonal pairs of any simple circuit. We might study these groups generally, but I propose here to restrict myself to groups in which all diagonal pairs are undistinguished from each other, so that they all belong to the same one-way simple network, say the *diagonal network*.

---

* **The investigation of sections 256–269 was suggested by the late Professor Clifford's paper on "Grassman's Extensive Algebra," in the 'American Journal of Mathematics,' vol. i., pp. 350–358.**

257. Every unit a is accompanied by one unit a', which makes with it a diagonal pair. We may term a' the *companion* of a. We have $(a')'=a$.

258. Let each pair of the diagonal network be represented by a π, then if α be an unsymmetrical pair of any simple network of unsymmetrical pairs, we have

$$\alpha^2=\pi, \quad \alpha^3=\alpha', \quad \alpha^4=1.$$

Also if β be a symmetrical pair we have $\beta^2=1$.

259. The network (π) is commutative with all the others of the group. For if α be any unsymmetrical pair we have $\alpha^2=\pi$, and therefore $\alpha\pi=\alpha\alpha\alpha=\pi\alpha$; and if β be any symmetrical pair, either there is no unsymmetrical pair in the group, every circuit being of period 2, in which case every pair is commutative with every other, or else there are unsymmetrical pairs $\lambda\lambda\ldots\mu\mu\ldots$, &c., in which case let

$$\beta\gamma=\lambda, \ \gamma\beta=\mu,$$

then

$$\pi\beta=\lambda^2\beta=\beta\gamma.\beta\gamma.\beta=\beta.\gamma\beta.\gamma\beta=\beta\mu^2=\beta\pi.$$

260. If α, β be any pairs, $\alpha\beta=\beta\alpha$ or $\beta\alpha\pi$. For let $\alpha\beta=\lambda$, and $\alpha\beta=\beta\alpha\sigma$, then

$$\lambda^2=\alpha\beta.\alpha\beta=\alpha\beta\beta\alpha.\sigma=\alpha 1\alpha.\sigma \text{ or } \alpha\pi\alpha.\sigma=\alpha^2\sigma \text{ or } \alpha^2\pi\sigma$$
$$=\sigma \text{ or } \pi\sigma.$$

But $\lambda^2=\pi$ or 1, therefore $\sigma=\pi$ or 1.

261. We have

$$\alpha\beta\gamma\delta=\alpha\gamma\beta\delta \text{ or } \alpha\gamma\beta\pi\delta$$
$$=\alpha\gamma\beta\delta \text{ or } \alpha\gamma\beta\delta\pi$$

according as

$$\beta\gamma=\gamma\beta \text{ or } \gamma\beta\pi$$

i.e., if we start from any given unit and proceed along a chain composed of pairs belonging to a given collection of networks, and then starting from the same unit proceed along a chain composed of pairs of the same kind but in a different order, we shall either arrive at the same unit as in the previous case or at its companion.

262. If we substitute for π the symbol -1, so that

$$\alpha'=\pi\alpha=-\alpha$$

we have, if β be a symmetrical pair, $\beta^2=1$; if unsymmetrical, $\beta^2=-1$. Also, if α and β be any two pairs, we have

$$\alpha\beta=\beta\alpha \text{ or } -\beta\alpha.$$

263. The group (No. 5 of sec. 248; see fig. 46*b*) of 8 units given by the following table:—

u	x'	y'	z'	u'	x	y	z
x'	u'	z	y'	x	u	z'	y
y'	z'	u'	x	y	z	u	x'
z'	y	x'	u'	z	y'	x	u
u'	x	y	z	u	x'	y'	z'
x	u	z'	y	x'	u'	z	y'
y	z	u	x'	y'	z'	u'	x
z	y'	x	u	z'	y	x'	u'

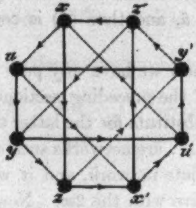


Fig. 46*b*.

is one of the species we are considering. The laws of multiplication of the component simple networks (sec. 234), viz. of

$$(ux),\ (ux'),\ (uy),\ (uy'),\ (uz),\ (uz'),\ (uu),\ (uu'),$$

(sec. 201) are the same as those of the quaternion expressions

$$i,\ -i,\ j,\ -j,\ k,\ -k,\ 1,\ -1.$$

For example, we have $uy >\!\!-\!\!\!-\!\!< xz$ and $uz >\!\!-\!\!\!-\!\!< zu'$, and thus, just as we have $ijk=-1$, so we have $(ux)(uy)(uz)=(ux)(xz)(zu')=(uu')$. I shall accordingly term the group a *quaternion* group.

264. A double network of which the detached portions (sec. 206) are each such as that shown in fig. 46*b* may be termed a *pure quaternion network*. The two component networks are non-commutative; each may be termed the *conjugate* of the other, and we may represent the conjugate of (α) by $(\bar{\alpha})$.

265. I proceed to show that every group of the family now under consideration may be defined by a pure complete network (sec. 235) consisting of m pairs of conjugate networks (*i.e.* m distinct quaternion networks), and r other simple networks having no conjugates in the network, ($2m+r$ simple networks in all); the $2m+r$ simple networks being such that each two are commutative unless they be a conjugate pair.

266. Consider a pure compound network consisting of m distinct pure quaternion networks. If P be any chain of the pairs composing the $2m$ simple networks, each sort of pair entering only once, if at all, into the chain, we have $\mathrm{P}\alpha=\alpha\mathrm{P}\pi$ or $\alpha\mathrm{P}$, *i.e.*, P non-commutative or commutative with α, according as the chain contains or does not contain a pair $\bar{\alpha}$. Now if (ν) be any simple network which is not one of the $2m$. (ν) will be commutative with some of the $2m$, and non-commutative with others. Let N be a chain containing one pair from each of the conjugates of those of the $2m$ networks with which (ν) is non-commutative, then the simple network $(\mathrm{N}\nu)$ (sec. 233)

is commutative with each of the $2m$. For if (a) one of the $2m$ is non-commutative with (ν), the chain N contains the pair $\bar{a}$, and thus (a) is non-commutative with (N) also, and therefore commutative with $(\mathrm{N}\nu)$; and if (a) is commutative with (ν), N does not contain $\bar{a}$, and thus (a) is commutative with (N) also, and therefore also with $(\mathrm{N}\nu)$.

267. Suppose now we have any pure complete network consisting of $2m$ networks such as the $2m$ of the preceding sections, and also of other simple networks (λ), (μ), (ν) . . . ; we can substitute for the latter the simple networks $(\mathrm{L}\lambda)$, $(\mathrm{M}\mu)$, $(\mathrm{N}\nu)$ . . . where the (L), (M), (N) . . . are networks such as the (N) of the last section, and we shall still have a pure complete network, and it will be such that the networks other than the $2m$ are commutative with the $2m$. Now these networks other than the $2m$ are either all commutative with each other, or else there are two at least which are not; in the latter case we may add such two to the $2m$ and get $2m+2$ such as the $2m$; we may then as before substitute for the remainder simple networks which are all commutative with the $2m+2$, and may repeat the process continually until the remaining networks other than the conjugate pairs are all commutative with each other.

268. Any group of the family we are considering is such that all the simple networks are commutative, or that two at least are not; in the latter case, if we take the two as conjugates, and take in others so as to constitute a pure complete network, we can proceed to deal with this in the mode we have just indicated. Thus in every case we can obtain a pure complete network containing n lots of two conjugate networks, and one lot of r commutative networks, the networks of each of the $(n+r)$ lots being commutative with those of the others. Either n or r may vanish.

269. If we make $n=4$ and $r=1$ we have a group of 16 units given by the following table :—

u	x'	y'	z'	u'	x	y	z	U	X′	Y′	Z′	U′	X	Y	Z
x'	u'	z	y'	x	u	z'	y	X′	U′	Z	Y′	X	U	Z′	Y
y'	z'	u'	x	y	z	u	x'	Y′	Z′	U′	X	Y	Z	U	X′
z'	y	x'	u'	z	y'	x	u	Z′	Y	X′	U′	Z	Y′	X	U
u'	x	y	z	u	x'	y'	z'	U′	X	Y	Z	U	X′	Y′	Z′
x	u	z'	y	x'	u'	z	y'	X	U	Z′	Y	X′	U′	Z	Y′
y	z	u	x'	y'	z'	u'	x	Y	Z	U	X′	Y′	Z′	U′	X
z	y'	x	u	z'	y	x'	u'	Z	Y′	X	U	Z′	Y	X′	U′
U	X′	Y′	Z′	U′	X	Y	Z	u	x'	y'	z'	u'	x	y	z
X′	U′	Z	Y′	X	U	Z′	Y	x'	u'	z	y'	x	u	z'	y
Y′	Z′	U′	X	Y	Z	U	X′	y'	z'	u'	x	y	z	u	x'
Z′	Y	X′	U′	Z	Y′	X	U	z'	y	x'	u'	z	y'	x	u
U′	X	Y	Z	U	X′	Y′	Z′	u'	x	y	z	u	x'	y'	z'
X	U	Z′	Y	X′	U′	Z	Y′	x	u	z'	y	x'	u'	z	y'
Y	Z	U	X′	Y′	Z′	U′	X	y	z	u	x'	y'	z'	u'	x
Z	Y′	X	U	Z′	Y	X′	U′	z	y'	x	u	z'	y	x'	u'

The component simple networks of this group, viz. :—

$$\begin{array}{cccccccc} (ux), & (ux'), & (uy), & (uy'), & (uz), & (uz'), & (uu), & (uu'), \\ (u\mathrm{X}), & (u\mathrm{X}'), & (u\mathrm{Y}), & (u\mathrm{Y}'), & (u\mathrm{Z}), & (u\mathrm{Z}'), & (u\mathrm{U}), & (u\mathrm{U}'), \end{array}$$

are subject to the same laws of multiplication as the bi-quaternion expressions

$$\begin{array}{cccccccc} i, & -i, & j, & -j, & k, & -k, & 1, & -1, \\ \omega i, & -\omega i, & \omega j, & -\omega j, & \omega k, & -\omega k, & \omega, & -\omega. \end{array}$$

R-adic Groups.

270. We may have a set such that the unified component r-ads constitute a group. We may call the set an *r-adic group.* If $r=1$ the set is an ordinary group.

271. In an r-adic group any r-ad may be made to correspond to any other r-ad, but the correspondence of two r-ads completely determines a self-correspondence of the set. Thus if the form of the set be known, any self-correspondence is fully represented by a two-row r-column constituent of the table.

272. In an r-adic group of n units the tabular representation has $\frac{\underline{|n}}{\underline{|n-r}}$ rows. For all $(r-1)$-ads are undistinguished, and there are $\frac{\underline{|n}}{\underline{|n-r+1}}$ of these, and while any one remains identically-correspondent the remaining $(n-r+1)$-ad has self-correspondences characteristic of a group, *i.e.*, has $(n-r-1)$ self-correspondences. Thus there are in all $(n-r-1)\ \frac{\underline{|n}}{\underline{|n-r-1}}=\frac{\underline{|n}}{\underline{|n-r}}$ self-correspondences of the group including the identical correspondence.

273. A correspondence of two undistinguished aspects of an r-adic group has not more than $r-1$ foci (sec. 122).

274. Let S be a system of which the units are the whole collection of points lying on a straight line, viz., a, b, c, d, ... Any aspect *abcd* . . . of S is what is usually termed the "range *abcd* . . . ." For the range *abcd* . . . we can by a homographic transformation substitute another range of the same points a, b, c, d, . . . , *i.e.*, another aspect of S. Employing all the various homographic transformations we get a set of aspects of S. Now, if we assume that this set is a single system, *i.e.*, that all aspects of S derived from *abcd* . . . by homographic transformations are undistinguished from *abcd* . . . and each other, but are distinguished from all aspects which cannot be derived from *abcd* . . . by such transformations; then S will be a triadic group. For we can by a proper homographic transformation substitute for any three units of S any other three units of S, but when this substitution is made, every other unit of S has a definite unit of S substituted for it.

Substitutions.

275. Each row of the tabular representation of a system is derived from each of the others by definite substitutions. Instead of writing down the various rows, we may give one only, and state the law or laws according to which the other rows are derived. Thus the form of a system $a, b, c, d, \ldots$ is given by merely writing down the letters representing the units of the system (since each letter appears only once, we may represent the units by the letters in place of their sorts), and stating the laws of substitution, in other words, the substitutions proper to the form (sec. 105).

276. Conversely, in considering a system of n letters, or other things, admitting of certain substitutions, we are considering a system of n units of a definite form.

277. The various arrays of letters considered when dealing with substitutions are thus aspects of a system.

278. When the arrays are regarded as units the substitutions will be represented by pairs; substitutions of the same sort by undistinguished pairs; similar substitutions by similar pairs (sec. 230).

279. The substitution of one aspect of a system for another, substitutes for a component collection of any form another component collection of the same form.

Algebras.

280. Consider the system V of $3n$ units arrived at by regarding as units the pairs connecting the units $a, b, c, d, \ldots$ of a system S of n units with the three distinguished units λ, μ, ν. If we adopt the method of representation of secs. 139 and 152 the units of V will be represented by—

$$\begin{array}{ccccc} (a\lambda) & (b\lambda) & (c\lambda) & . & . \\ (a\mu) & (b\mu) & (c\mu) & . & . \quad \&c. \\ (a\nu) & (b\nu) & (c\nu) & . & . \end{array}$$

It will, however, conduce to clearness in the present instance to write them thus—

$$\begin{array}{ccccc} a_\lambda & b_\lambda & c_\lambda & . & . \\ a_\mu & b_\mu & c_\mu & . & . \quad \&c. \\ a_\nu & b_\nu & c_\nu & . & . \end{array}$$

The symbols of the three rows represent the units of three different systems, each of which systems is a replica of the others and of S. We may denote the three systems when regarded as units by S_λ, S_μ, S_ν, respectively.

281. Now consider the system E arrived at by regarding the triads connecting the three systems as units. This will contain n^3 units, which may be written thus— $(a_\lambda a_\mu a_\nu)$, $(a_\lambda b_\mu c_\nu)$, &c.

282. We have collections of triads connecting $S_\lambda S_\mu S_\nu$.[*] in which each pair connecting S_λ and S_μ appears once in a triad, and once only, *e.g.*, if S contains two units a, b, only, we have such collections as

$$\begin{array}{c} a_\lambda\, a_\mu\, a_\nu \\ a_\lambda\, b_\mu\, a_\nu \\ b_\lambda\, a_\mu\, a_\nu \\ b_\lambda\, b_\mu\, a_\nu \end{array} \quad \text{or} \quad \begin{array}{c} a_\lambda\, a_\mu\, b_\nu \\ a_\lambda\, b_\mu\, a_\nu \\ b_\lambda\, a_\mu\, b_\nu \\ b_\lambda\, b_\mu\, a_\nu \end{array} \quad \text{or} \quad \begin{array}{c} a_\lambda\, a_\mu\, b_\nu \\ a_\lambda\, b_\mu\, b_\nu \\ b_\lambda\, a_\mu\, b_\nu \\ b_\lambda\, b_\mu\, a_\nu \end{array}$$

The number of such collections in the general case is n^{n^2}, each containing n^2 triads. When the triads are regarded as units we get n^{n^2} collections each containing n^2 units of E.

283. When these collections are unified we get a system A of n^{n^2} units, which will be a multiple system.

284. The form of A is in part independent of that of S and in part dependent, certain components being distinguished whatever be the form of S, while it depends on what the form of S is whether others are distinguished or not.

285. When considering the multiplicity of the system A, or those peculiarities of form it possesses which arise from the mode of its construction apart from any special peculiarities in the form of S, we regard S as a single heap system.

286. If S be a single heap system, certain units of A are undistinguished from each other, while others are distinguished. If S be not a single heap system, so that its self-correspondences are more restricted than they would be in the former case, some units of A originally undistinguished become distinguished, so that a unit which was one of several undistinguished units, may become unique. Thus certain units of A have definite relations to S, and are of use as auxiliaries to the latter.

287. A convenient mode of conceiving of the system E is to regard its units as small cubes composing a big one, the axes of the cube being represented by λ, μ, and ν. Any layer of the cube normal to λ, say a λ layer, contains small cubes representing triads (unified) all containing the same unit of S_λ, and similarly in the cases of μ and ν. If a_λ be the unit of S_λ in the triads which are represented when unified by a λ layer, the layer may be termed the a_λ layer, and when unified represents a_λ. We may also conveniently term a row of cubes parallel to the axis λ a $\mu\nu$ row; it contains cubes representing triads all of which contain the same connecting pair of S_μ and S_ν, say the pair $a_\mu b_\nu$, and when unified is represented by $(a_\mu b_\nu)$. The λ layers thus represent the system S_λ, and must be supposed to admit of substitutions among themselves characteristic of the form of S_λ (sec. 276), and similarly in the case of μ and ν. Here the collection of units, which when unified gives a unit of A, is represented by cubes

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[*] In strictness this should be "triads connecting the systems which when unified are S_λ, S_μ, S_ν respectively;" but the abbreviation is convenient and will not lead to misconception (see sec. 20).

such that each $\lambda\mu$ row contains one cube and one only of the collection. If S be a single heap system, the multiplicity of A will be the number of the systems into which the collections of cubes thus constituted break up.

288. We may represent any one of the collections which when unified is a unit of A by a square diagram. Take, for example, the case $n = 4$; we have such a diagram as the following :—

	a	*b*	*c*	*d*
a	*a*	*d*	*b*	*d*
b	*c*	*c*	*a*	*b*
c	*b*	*a*	*c*	*d*
d	*d*	*b*	*a*	*a*

Here the square may be supposed to be a face of the cube normal to ν, λ and μ being supposed to be vertical and horizontal respectively. The left hand letters indicate whether the adjacent λ layers are a_λ or b_λ or c_λ, &c., respectively, the top letters whether the adjacent μ layers are a_μ or b_μ or c_μ &c., respectively; and the letters contained in the squares, each of which squares is supposed to represent a cube, *i.e.*, a unit of E, indicate which ν layers the various cubes lie in.

289. By regarding the pairs connecting the system E and a system of units π, ω, ξ, &c., which are all distinguished from each other, as unified, we may get a number of systems E_π, E_ω, E_ξ, &c., replicas of each other and of E, and we may consider systems arrived at by taking one or more component systems of each of the systems E_π, E_ω, E_ξ, &c. Similarly in the case of A.

290. Now let α be one of the units of A arrived at by regarding as unified a collection of units of E of which $(a_\lambda b_\mu c_\nu)$ is one. This collection of units of E which when unified is α, contains no other unified triad of the sort $(a_\lambda b_\mu \cdot)$, *e.g.*, $(a_\lambda b_\mu d_\nu)$, so that c_ν is unique with respect to α, a_λ, b_μ; for when c_ν is changed to d_ν, a_λ and b_μ remaining unchanged, α is changed to a unit arrived at by regarding a collection of units of E containing $(a_\lambda b_\mu d_\nu)$ as unified, which cannot be α. We may, therefore, write

$$c_\nu = (\alpha a_\lambda b_\mu).$$

We may deal with the other triads concerned in arriving at α in the same way, and get a collection of n^2 equations, viz.—

$$\begin{array}{lll}
(\alpha a_\lambda a_\mu) = . & (\alpha b_\lambda a_\mu) = . & \\
(\alpha a_\lambda b_\mu) = c_\nu & (\alpha b_\lambda b_\mu) = . & \text{\&c.} \\
(\alpha a_\lambda c_\mu) = . & (\alpha b_\lambda c_\mu) = . & \\
\text{\&c.} & \text{\&c.} & \text{\&c.}
\end{array}$$

where the letters on the right-hand side of the equations depend on the particular unit α selected.

291. Now we may make $c_\pi \equiv c$, and similarly in the case of every other unit of S and S_π; also we may represent the units λ and μ by two *positions*, and write $a_\lambda b_\mu$ thus $a_1 b_2$, where the order of a_1 and b_2 is immaterial, or merely ab where the order is material; the equations then become

$$\begin{array}{lll} (\alpha aa) = . & (\alpha ba) = . & \\ (\alpha ab) = c & (\alpha bb) = . & \&c. \\ (\alpha ac) = . & (\alpha bc) = . & \\ \&c. & \&c. & \&c. \end{array}$$

If then we have two equations such as

$$(\alpha ab) = c \text{ and } (\alpha cd) = e,$$

we may write

$$e = (\alpha(\alpha ab)d),$$

and similarly in other cases; so that we obtain complex expressions representing the form relations which the units of S hold to each other and to the units λ, μ, α; which expressions, however, admit of considerable simplification in certain cases.

292. An equation such as $(\alpha ab) = c$ I shall term a *primitive equation.* The whole collection of triads which are concerned in arriving at α will be termed a *primitive algebra*, α being termed a *unified primitive algebra.*[*] An equation, such as $e = (\alpha(\alpha ab)d)$, where only one primitive algebra is involved, may be termed a *complex primitive equation.*

293. Those components of E which are represented when unified by the units of A furnish us, by the application of the preceding methods, with every possible primitive algebra, associative or non-associative, commutative or non-commutative, &c., and we can discuss the number of the forms, and the relations of the various algebras, by discussing E in the case in which S is a single heap system (sec. 285).

294. We may have any number of unified primitive algebras α, β, γ, δ, . . . which may be undistinguished from each other or not. If the unified primitive algebras are all selected from one system A_π (sec. 289), they may be said to be algebras of the *same operation* π, if from different systems A_π, A_ω, they may be said to be algebras of different operations, *e.g.*, multiplication, addition, &c.

295. We may deal with each of these algebras as with α and we may also deal with them in combination and obtain equations such as $e = (\alpha(\beta ab)d)$, giving complicated expressions for the units of S, which will represent the form relations they hold to each other and to the units λ, μ, α, β, &c.

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[*] We might regard the primitive equations as units, and apply the term "unified primitive algebra," not to α, but to the unit arrived at by regarding as unified the collection of unified primitive equations derived from the triads concerned in arriving at α.

296. Where two or more primitive algebras are considered, we may speak of the unit arrived at by regarding them as unified as a *unified compound algebra.*

297. The discussion of form is very generally carried on by the help of these auxiliary algebras. In some cases the units $a, b, c, d, \ldots$ of the base system under consideration are regarded as unified pairs $\mathrm{X}a'$, $\mathrm{X}b'$, $\mathrm{X}c', \ldots$ where X is an algebra primitive or compound, and $a', b', c', \ldots$ are units constituting a single heap system, which have the correspondences characteristic of the system $a, b, c, \ldots$ as long as X remains identically correspondent. But various devices exist which must be examined in each case.

298. Where only one unified primitive algebra is considered, we may regard the unit α as expressed by the brackets ( ), and write an equation $(\alpha ab)=c$ simply as $(ab)=c$, or we may omit the brackets and write the equation thus $ab=c$.

299. If in an algebra every equation $(ab)=c$ is accompanied by an equation $(ba)=c$, the algebra is said to be *commutative.*

300. If in an algebra any three equations such as

$$\begin{array}{c}(ab)=x\\(bc)=y\\(xc)=z\end{array}$$

are accompanied by the equation

$$(ay)=z$$

the algebra is said to be *associative.* Since $((ab)\ c)=(a(bc))$ either expression may be written (abc), and no ambiguity arises.

301. If π and ρ two algebras are such that the equations

$$\begin{array}{cc}(\pi ab)=x & (\pi ba)=l\\(\pi ac)=y & (\pi ca)=m\\(\pi ad)=z & (\pi da)=n\end{array}$$

$$(\rho bc)=d$$

are accompanied by the equations

$$\begin{array}{cc}(\rho xy)=z & (\rho lm)=n\end{array}$$

i.e., if $\rho\ (\pi ab\ .\ \pi ac)=\pi\ (a\ .\ \rho bc)$

and $\rho\ (\pi ba\ .\ \pi ca)=\pi\ (\rho bc\ .\ a)$

then the algebra π is said to be *distributive* with respect to the algebra ρ.

We may take πab to be $a\times b$, and ρab to be $a+b$; we then have

$$\begin{array}{c}a\times b+a\times c=a(b+c)\\b\times a+c\times a=(b+c)\times a\end{array}$$

302. An algebra may be *self-distributive*, *i.e.*, such that

$$(a(bc))=((ab)(ac)).$$

(See sec. 349.)

303. An important class of primitive algebras is that in which $(ab) \neq a$ or b, except in the case of one unit z, which is such that $(zz)=z$, and also such that whatever unit of S a may be $(za)=a$ and $(az)=a$. Here every unit a is accompanied by another a' such that $(aa')=z$. Ordinary addition and multiplication furnish two such algebras. In the former (ab) is $a+b$, a is 0, and a' is $-a$; in the latter (ab) is $a\times b$, z is 1, and a' is $\frac{1}{a}$.

304. The algebras which are such that in the case of each unit a we have $(aa)=a$, are also of considerable importance. We have such an algebra in the case of ordinary logic (sec. 360).

305. We may in ordinary parlance speak of three units a_λ, b_μ, c_ν, composing the triad giving rise to a primitive equation, as if they were units a, b, c, of S, without any ambiguity arising. The unit a when dealt with as a multiplier will be a_λ, and so on; but it will not be necessary to be continually pointing this out. We may thus speak of products (aa) when there is really only one a.

306. If in any system of units S every pair is accompanied by one or more units unique with respect to the pair, we may select one of these accompanying units in the case of each pair and term it the *product* of the pair. Where there is only one such accompanying unit in the case of each pair, this will be the product, but if there be several such, any one of these might be chosen as the product. The most natural mode of selection in the case of undistinguished pairs is to select products which will with the pairs make undistinguished triads. (Secs. 343, 349.)

307. In the case of distinguished pairs we cannot of course do this, but we may in some cases choose products so that the resulting triads will all be of the same form, this not being so if other products be chosen; or we may choose the products, so that by ignoring some difference the triads all become undistinguished from each other, the products still being unique with respect to the pairs.

308. In cases in which some pairs are not accompanied by a unit unique with respect to them, or even in other cases, we may add to S a single system of one unit Z, and call this the product of the pairs; Z being also considered as the product of each unit of S when multiplied by or into Z. (Sec. 319, and *cf.* sec. 343.)

309. In certain cases the products considered may not be unique with respect to the multiplier and multiplicand, but with respect to a collection containing them and certain other units, which remain the same in the case of every multiplier and multiplicand of the system, and may therefore be termed *constants*.

An instructive example of this is furnished by a system of collinear points. If i, z, u, a, b, be five points of such a system, there is one point, and one only, which is such that the six points

$$i, z, u, c, a, b,$$

lie respectively on the six lines

$$PQ, RS, PR, QS, PS, QR,$$

passing through four coplanar points P, Q, R, S : *i.e.*, the unit c is unique with respect to the collection i, z, u, a, b. Now let i, z, u, be three *constants* in the foregoing sense. Then we may call c the *product* of a and b. The primitive algebra which thus arises may readily be shown to be associative and commutative.

Again, there is one point d, and one only, which is such that the points

$$i, i, z, d, a, b,$$

lie respectively on the six lines

$$LM, NO, LN, MO, LO, MN,$$

passing through four coplanar points L, M, N, O : *i.e.*, the unit d is unique with respect to the collection i, z, a, b. Here, if i and z be constants, d may be regarded as a second species of product of a and b, and may be termed the *sum* of a and b. The primitive algebra thus arising is also associative and commutative.

The first of these two primitive algebras is distributive as regards the second. In fact the compound algebra composed of the two primitive algebras is of the same kind as the ordinary algebra of quantity, the units i, z, u, corresponding respectively to the ∞, 0, and 1 of such algebra.*

310. We may speak of the collection consisting of the products of the pairs connecting two component collections of a system S as the product of those collections. If the number of units in the multiplier collection be n, and the number of those in the multiplicand be m, the number in the product will not necessarily be mn, for the product x of a connecting pair ap may be the same unit as the product of another connecting pair bq. We may speak of the collection consisting of the products of all the pairs of a collection $a, b, c, d \ldots$ together with the products (aa), (bb), $(cc) \ldots$ as the square of the collection $a, b, c, d \ldots$ In the same way we may have cubes, &c., of a collection.

311. If we substitute for S the system S_n of sec. 191, we may regard products (ap) and (bq) as two different units (sec. 192), and if this be done in the case of each product, we shall have mn units in the product.

312. We may regard the components of S or S_n as units, and then the products will be units, the products of pairs of units.

Quadrates.

313. Let S_1, S_2, be two single heap systems, replicas of each other. Let $a_1, b_1, c_1 \ldots$ be units of S_1; $a_2, b_2, c_2 \ldots$ be corresponding units of S_2. Considering the pairs connecting S_1 and S_2; these may be written

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* See a paper by the writer "On an Extension of Ordinary Algebra" in the *Messenger of Mathematics*. Vol. XV. New Series, p. 188.

$$\begin{array}{lll} a_1\, a_2 & a_1\, b_2 & a_1\, c_2, \text{ \&c.} \\ b_1\, a_2 & b_1\, b_2 & b_1\, c_2, \text{ \&c.} \\ c_1\, a_2 & c_1\, b_2 & c_1\, c_2, \text{ \&c.} \\ \text{\&c.} & \text{\&c.} & \text{\&c.} \end{array}$$

If it be understood that we are throughout dealing with pairs connecting S_1S_2 we may write any aspect $p_1\, q_2$ thus pq, the position of a letter in the pair taking the place of the unit represented by the subscript number. We then have under consideration the aspects

$$\left.\begin{array}{lll} aa & ab & ac, \text{ \&c.} \\ ba & bb & bc, \text{ \&c.} \\ ca & cb & cc, \text{ \&c.} \\ \text{\&c.} & \text{\&c.} & \text{\&c.} \end{array}\right\}\ldots\ldots(X)$$

These will be n^2 in number, where n is the number of units in each of the systems S_1 S_2. The aspects aa, bb, cc, . . . are undistinguished from each other, but are distinguished from all the other aspects ab, ac, bc . . . . which again are all undistinguished from each other.*

314. We may regard the aspects as unified, and shall then get a double system P composed of the system P_1 of n unified aspects (aa), (bb), (cc) . . . . ., and the system P_2 of n^2-n unified aspects (ab), (ac), (bc) . . . . †

315. The mode of arranging the aspects adopted at X in sec. 313 suggests a mode of clothing the units of P which is very convenient for purposes of description, and for emphasizing the peculiarities of P; viz., that of regarding the units as arranged in rows and columns, the order of which is to be disregarded, so that the rows as units form a single heap system, as also the columns.

316. In fig. 60 we have a system P of the species considered, in which $n=4$; the asterisks represent units of P_1, the dots those of P_2.

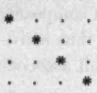
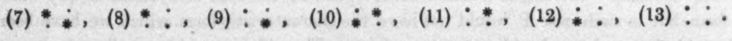


Fig. 60.

317. The pairs of P form a system of multiplicity 13; viz., we have the 13 sorts of pairs given by the following diagrams, where in the last seven cases the top unit in the first column, and the bottom in the second are those composing the pair considered.



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* If we confine ourselves to the latter system of aspects, we might regard them as aspects of either of the systems S_1 and S_2; but the aspects aa, bb, cc . . . . must be regarded as connecting pairs of the two systems S_1 and S_2.

† We should obtain a system of the same form as P if we took S_1, and the unified pairs of S_1. Here S_1 takes the place of P_1, and the unified pairs of S take the place of P_2.

The pairs (1), (5), (10), and (12) will be termed *joined* pairs; each is such that the column in which the first unit lies and the row in which the second unit lies intersect at an asterisk. In the literal mode of representation they are such as

$$(1)\ (aa)(ab),\quad (5)\ (ba)(aa),\quad (10)\ (ab)(ba),\quad (12)\ (ab)(bc),$$

i.e., such that the last letter in the first bracket is of the same sort as the first letter in the last bracket. We may add to these the pairs such as $(aa)(aa)$ which are really connecting pairs of two systems P_λ and P_μ. The pairs (2), (3), (4), (6), (7), (8), (11), may be called *unjoined* pairs.

318. Each joined pair is accompanied by a unit unique with respect to it, represented by the dot or asterisk in the same row as the dot or asterisk representing the first unit of the pair, and in the same column as the dot or asterisk representing the second unit of the pair. This unit may be taken as the product of the two units composing the pair. In the literal mode of representation we shall have

$$(ab)(bc)=(ac)$$

where a, b, c, or any two of them may be letters of the same sort.

319. The product of two unjoined pairs is taken to be a unit Z or 0, and if (ab) be any unit of P, we take

$$(ab)\mathrm{Z}=\mathrm{Z}$$
$$\mathrm{Z}(ab)=\mathrm{Z}$$
$$\mathrm{ZZ}\ \ =\mathrm{Z}\ \text{(sec. 308).}$$

320. The units (ab), (ac), (bc), . . . , when thus dealt with as multipliers, multiplicands, and products, the products being those specified in the preceding sections, may be called *quadrates*.*

321. We may consider products of component collections of P or P_H (sec. 311); and we may regard these as unified, and thus arrive at various primitive algebras.

322. These quadrate algebras are all associative.

323. It will be convenient in many cases to write a quadrate (ab) thus $\frac{a}{b}$, assimilating it to the ordinary algebraic fraction, and a collection of quadrates (sec. 321) thus, $\frac{a}{b}+\frac{b}{c}+\frac{b}{d}$.

324. Quadrates have been arrived at by considering unified pairs in the case of single-heap systems. We might consider unified pairs in the case of systems of any other form, but in such case P would not have the characteristic form which we have been considering, and we should not get products. Thus if we considered discrete heaps, all the unified pairs would be distinguished from each other. We, of course, can and do consider, unified pairs of any system S, and can take their products as if they were

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* See PIERCE on "Linear Associative Algebras," in the 'American Journal of Mathematics,' vol. iv., p. 215.

quadrates; but in such case we ignore differences, and do not deal with S, but with a single heap system of the same number of units (secs. 127, 128). The special form of S has its effect as the selector of special quadrates, or collections of quadrates (sec. 321).

325. Thus if S be a group the unified pairs divide up into systems, and we naturally select these. The product of two such systems of unified pairs is another such system. The unified systems (which are represented by the sorts of the pairs) give us a primitive associative algebra. The equations we obtain are precisely the same as those we should get if we considered chains in the manner indicated in section 234. In both instances the equations exhibit relations existing between sorts of letters, which in both instances represent simple networks. In the one instance we arrive at these relations by considering individual component pairs of simple networks, in the other by considering the whole systems of pairs composing those networks.

326. The unified aspects of any system S are a group. The unified pairs of these are substitutions by which any aspect of S is substituted for another. The product of any two of these is a substitution proper to S (sec. 105), viz., that which results from operating with the multiplier and multiplicand in succession.

327. A substitution proper to S is represented by a two-row constituent of the tabular representation of S. Each column of this constituent may be regarded as a quadrate, the whole constituent being thus regarded as a collection of quadrates. Thus a substitution may be represented either by a collection of quadrates obtained by taking pairs of S, or by a collection of quadrates obtained by taking pairs of the group of which the units are unified aspects of S.

Isolated Collections—Residuals—Satisfied Collections.

328. A collection of units which is such that each unit of the collection is unique with respect to the residue of the collection may be said to be *isolated*. Each unit of the collection may be termed the *residual* of the rest.

329. The residual of a pair a, b may be written (ab) (sec. 139), and similarly in the case of triads, &c.

330. We may graphically represent an isolated triad as in fig. 61, where λ is an

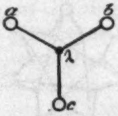

Fig. 61.

auxiliary graphical unit; a non-isolated triad being represented as in fig. 62, without links or auxiliary units. The same mode of representation may also be applied in the case of isolated n-ads where $n \neq 3$.

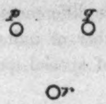

Fig. 62.

331. Where we are considering residuals of collections of r units, if a collection of units C is such that every component collection of r units has one and only one residual, which residual is also a component of the collection C, then C may be said to be *satisfied.*

Some Isolated-Triad Systems.—Family No. 1.

332. There are certain systems in which every component collection of two units has one residual and one only. One such system is met with in the case of the points of intersection of a plane cubic with coplanar straight lines; these make isolated triads of collinear points such that if a, b, c; d, e, f; g, h, i; a, d, g; b, e, h are isolated triads, c, f, i is one also; *i.e.*, we have $((ab)(de)) = ((ad)(be))$.

333. In another which I shall now consider the law of distribution of the isolated triads is such that if p, q, r, be a non-isolated triad; and if l be the residual of q, r; m of r, p; n of p, q; then l, m, n is an isolated triad; *i.e.*, we have $((pm)l) = (p(ml))$.

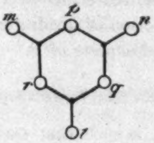

Fig. 63.

334. It is an immediate consequence of the law of distribution of sec. 333, that if s be the residual of l, p (fig. 63), it is also the residual of m, q and n, r. Thus we arrive at a collection of 7 units (comprising the isolated triads l, m, n; m, r, p; r, l, q; p, q, n; p, l, s; q, m, s; r, n, s), which contains the residual of each of its component pairs and is therefore satisfied. The whole collection is shown in fig. 64.

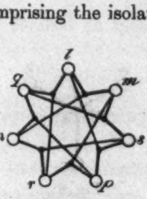

Fig. 64.

335. In a system of this species, if we add a unit to a satisfied collection C of m units, we must also add m others, getting $2m+1$ in all, before we can get a satisfied collection. This may be thus shown :—Let $a, b, c, d, \ldots .$ be the units of C, and let a unit u be added to C, and let $a', b', c', \ldots .$ be the residuals of u, a; u, b; u, c; $\ldots .$ respectively; then $a', b', c', \ldots$ must all be different units; for if a' and b' were identical we should have both u, a', a, and u, a', b, isolated triads. If then a unit u be added to C, m others $a', b', c', d', \ldots$ must also be added, making $2m+1$ in all. This collection of units will be satisfied, so that we need not add any more units. To prove this we have only to show that the residual of b', c', any two added units is a unit of the enlarged collection. Let the residual of b, c, which will be a unit of C be a, then we have the non-satisfied triad u, b, c, and the residuals of its pairs are b', c', and a which by sec. 333 form a satisfied, or isolated triad, for they are the same thing, so that the residual of b', c', is a.

336. Now every non-satisfied triad is a component of a satisfied collection of seven units; and by the preceding section if there be another unit added we get a collection of 15 units, if again another be added one of 31 units, and generally a satisfied collection consists of 2^n-1 units. Every system of the species considered is of course satisfied, and therefore contains 2^n-1 units.

337. If to any component collection C of one of these systems we add such residuals of the different component pairs as are not already in C, and repeat the process on the enlarged collection we get a definite satisfied component. The component R which consists of all the added units may be termed the *complement* of C. The complement of any pair is their residual. If C be itself satisfied there will be no complement. It does not follow if R be the complement of C, that C is the complement of R, though the complement of R must be a component of C. Thus the complement of p, q, n, s, l, in fig. 64 is m, r, but the complement of m, r is p.

338. Consider a system S of the family containing 2^n-1 units. Take any pair of S, add to it any unit of S not the residual, add to the resulting triad any unit of S not in its complement, add to the resulting tetrad any unit of S not in its complement, and so on. Proceeding in this way we get an n-ad, one of several, such that its complement comprises all the remaining units of S. The components of three, four, &c., units of the n-ad may be termed *principal* triads, tetrads, &c., of S. A principal n-ad has the same self-correspondences as a single heap of n units.

339. Let $a, b, c, d \ldots . k, l$ be a principal component of a system S, substitute for a, b their residual γ, for γ and c their residual δ, for δ and d their residual ϵ, and so on until we get the pair λ, l, for which substitute their residual μ, which will be unique with respect to $a, b, c, d \ldots . k, l$. We should arrive at μ if we took the units of the component in any other order. To show this it is only necessary to prove it for an interchange of any two units, for by a succession of such interchanges we can pass to any fresh order. Let us then interchange any two units c and d, and let ξ be the residual of γ, d, then we have to show that ϵ is the residual of ξ, c. This

follows at once from the law of sec. 333, for γ, δ, d is a non-isolated triad and γ, δ, c, δ, d, ϵ, and d, γ, ξ are isolated; thus c, ϵ, ξ is isolated and ϵ is the residual of ξ, c. We should arrive at μ if we were at any stage to substitute the residual of *any* two units of the reduced component, instead of always taking the last substituted residual as one of the two; *e.g.*, after substituting δ for γ, c, we might substitute the residual of h, k for h, k. The unit μ is clearly a component of the complement of $a, b, c, d \ldots . k, l$. It is obvious that if we started with the component $a, b, c, d \ldots . k, \mu$ we should arrive at the unit l, and generally any other unit of $a, b, c, d \ldots . k, l, \mu$ would be arrived at from the rest. In fact the whole collection $a, b, c, d \ldots . k, l, \mu$ is isolated, and each unit is thus a residual of the remainder, the only one that there is.

340. The process of the preceding section may be applied to any component whatever of S, with this modification in the case of non-principal components, viz., that where the residual of any pair is included in the component so that we cannot add it to the latter in substitution for the pair, in such case the whole triad must be removed from the component. This amounts to removing any isolated r-ad which is contained in the component. If in the result one unit remains, it will be the only residual; if no unit remains the component is isolated.

341. We may classify the units of S relatively to a principal component of n units thus, viz., we have

(1) The principal component of	n	units
(2) The residuals of the pairs of these	$\dfrac{\lvert\underline{n}}{\lvert\underline{2}\,\lvert\underline{n-2}}$	in number
(3) ,, ,, triads	$\dfrac{\lvert\underline{n}}{\lvert\underline{3}\,\lvert\underline{n-3}}$	,,
(4) ,, ,, tetrads	$\dfrac{\lvert\underline{n}}{\lvert\underline{4}\,\lvert\underline{n-4}}$	,,
(r) ,, ,, r-ads	$\dfrac{\lvert\underline{n}}{\lvert\underline{r}\,\lvert\underline{n-r}}$	,,
. . . .	. .	. .
(n) The residual of the n units	1	,,
Total	2^n-1	units.

342. If we represent the units of the principal component (1) by the letters $a, b, c, \ldots$, we may represent every other unit of S as a residual of two or more of these in the manner indicated in sec. 329. The order of the letters in the brackets will be immaterial. The symbol representing the residual of any two units of S will be arrived at by aggregating the letters contained in one or other of the two symbols

representing the two units, but not in both; *e.g.*, the product of $(abcd)$ and (cde) will be (abe).

343. If we call the residual (ab) the product of a and b, and add to S a system of one unit 1 such that

$$(aa)=1$$

$$(a1)=a$$

whatever unit of S a may be (*cf.* sec. 308), we have an algebra subject to the associative law, viz., we have

$$((ab).c)=(a.(bc))$$

Some Isolated-Triad Systems.—Family No. 2.

344. Another distribution of isolated triads which may exist is this:—If a, b, c, be an isolated triad, and if o, a, l; o, b, m; o, c, n are also isolated triads, then l, m, n is an isolated triad. Thus $((oa)(ob))=(oc)=(o(ab))$.

345. Here, if a, b, c, d . . . . be any satisfied component of the system, and a unit o be added, the residuals (oa), (ob), (oc) . . . . will also compose a satisfied collection, the triad (oa), (ob), (oc), being isolated or not according as a, b, c is an isolated triad, or not.

346. The various residuals $(a(oa))$ or o, $(a(ob))$, $(a(oc))$ . . . . are all distinct units, no two of these symbols denoting the same unit; and they constitute a satisfied collection, the triad $(a(ob))$, $(a(oc))$, $(a(od))$ being isolated or not according as (ob), (oc), (od) is isolated or not, *i.e.*, according as b, c, d, is isolated or not; and similarly in the case of the residuals $(b(oa))$, $(b(ob))$ . . . . .

347. We have $(a(ob))=((ao)(ab))$ (sec. 344), and thus the united collections

a, b, c . . . . .
(oa), (ob), (oc) . . . .
$(a(oa))$, $(b(oa))$, $(c(oa))$ . . . . .

constitute a satisfied collection. If the number of units in the collection a, b, c, ... is n, the total number in the satisfied collection arrived at by adding o is $3n$.

348. Thus the total number of units in any satisfied collection of the species now under consideration is 3^n.

349. If we call the residual (ab) the *product* of a and b, and write it for simplicity ab, we see that $ab.c \neq a.bc$, so that the associative law does not hold, as in the preceding systems. But we have $a.bc = ab.ac$, so that the algebra is self-distributive. We can have, as in the case of the preceding family of systems,

$$aa=1$$

$$a1=1.$$

Geometry in General.

350. In most geometrical investigations the units constitute a system of a high order of multiplicity; we have points, straight lines, conics, cubics, &c., unified collections of two, three, or more of these, operators such as quarternions, &c., &c., &c. It will, however, be sufficient for the purpose of illustration to refer briefly to some comparatively simple systems.

351. It is to be understood that points and the line at infinity are not regarded as distinguished from other points and lines, and consequently parallelism is looked upon merely as intersection on a particular line.

System of Coplanar Points and Straight Lines.

352. In a general consideration of coplanar points and straight lines the points compose a single system, being undistinguished from each other, and the same thing is the case with the straight lines. The connecting pairs of the two systems are of two sorts, for a point may either lie on a line or off it; and, as there is no other special relation between a point and a line, the system of connecting pairs is a double one.

353. We may graphically represent the lines by the graphical units ○ ○ ○ ○, and the points by the graphical units • • • • •. If a point lies on a line we may connect the corresponding graphical units by a link thus ○——•, no link being drawn in the other case.

354. The number of points on each line is infinite, and an infinite number of lines pass through each point. Every two points lie on one line and one only, so that if *a* and *b* are any two points, the line P which is linked to both is unique with respect to *a*, *b* (fig. 65). Pairs of points are accordingly all undistinguished from each other.

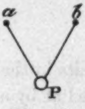

Fig. 65.

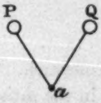

Fig. 66.

355. Every two lines pass through one common point, and one only; so that if there is a point *a* linked to two lines P and Q, *a* is unique with respect to PQ (fig. 66).

356. Every form which component collections of lines and points possess is also possessed by component collections of points and lines; the two component single systems being of precisely the same form.

357. We may take as fundamental laws defining the distribution of the links, and therefore the form of the double system the two well-known theorems:

(1.) If the three points in each of the nine triads of points

$$a, b, c;\quad a, d, e;\quad a, g, f;\quad b, d, h;\quad c, e, h;\quad d, f, l;\quad e, g, l;\quad b, f, k;\quad c, g, k.$$

are collinear, the points of the triad h, k, l are also collinear (fig. 67).

(2.) If the three points in each of the eight triads of points

$$a, b, c;\quad a, h, f;\quad d, e, f;\quad a, g, e;\quad b, g, d;\quad c, h, d;\quad b, k, f;\quad c, k, e$$

are collinear, the points in the triad g, h, k are also collinear (fig. 68).

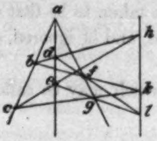

Fig. 67.

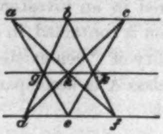

Fig. 68.

Coplanar Points, Lines, and Conics.

358. In the case of the treble system composed of coplanar points, straight lines, and conics, each line touches, cuts, or does not touch or cut each conic, and each point lies on, in, or outside each conic; we thus have three sorts of connecting pairs in each case. We may conveniently connect the graphical unit representing a conic by links to the graphical units representing points lying on the conic, and to the graphical units representing lines touching the conic; no links being drawn in the other cases; so that the unlinked pairs are a double system.

359. If a be any point, C any conic, of the system, there is one line and one line only of the system which is unique with respect to the pair a, C, viz., the polar λ of a with respect to C. Likewise a is the only point unique with respect to λ, C.

Logic.

360. It will be convenient to approach the consideration of Formal Logic from the standpoint of the algebraist. Classes are denoted by terms A, B, C, D, . . . The class which just contains, and the class which is just contained in, all the classes A, B, C, are denoted respectively by the sum A+B+C, and the product ABC of the terms denoting the several classes. Whatever class A may be, we have AA=A, and A+A=A. Addition and multiplication are each commutative and associative; and are also distributive as regards each other, so that we have

$$(A+B)(C+D)=AC+AD+BC+BD$$
$$AB+CD=(A+C)(A+D)(B+C)(B+D)$$

If AB=A, which implies also A+B=B, then A is contained in B.

361. Two classes U and Z are considered which are such that whatever class A may be, we have

$$\mathrm{U}+\mathrm{A}=\mathrm{U}, \text{ and therefore also } \mathrm{UA}=\mathrm{A}$$
$$\mathrm{Z}+\mathrm{A}=\mathrm{A}, \text{ and therefore also } \mathrm{ZA}=\mathrm{Z}$$

so that U contains every class, and Z is contained in every class. U is the class called the "universe," Z is that called the "non-existent" class. The class U need not be taken as the actual universe of thought, but as that class which contains all classes considered in an investigation. So Z may be taken to be that class which in any investigation is contained in all others considered, and is ignored, or regarded as having the quality of "non-existence."

362. Every class A is accompanied by a class A′ which may be called its *obverse*, and is such that

$$\mathrm{A}+\mathrm{A}'=\mathrm{U}$$
$$\mathrm{AA}'=\mathrm{Z}$$

so that A is the obverse of A′. A′ is "not A." U and Z are obverses of each other. We have

$$(\mathrm{A}+\mathrm{B}+\mathrm{C}+\mathrm{D}+\ldots)'=\mathrm{A}'\mathrm{B}'\mathrm{C}'\mathrm{D}'\ldots$$
$$(\mathrm{ABCD}\ldots)'=\mathrm{A}'+\mathrm{B}'+\mathrm{C}'+\mathrm{D}'+\ldots$$

363. Now, consider a collection of n classes a, b, c, d, . . . such that the product of every two is a class z; *i.e.*, such that no two classes of the collection have any part in common except that which is common to all the classes, and may therefore, when our attention is confined to the classes of the collection and their aggregates, be regarded as immaterial, and therefore be treated as non-existent. Such a collection may be said to consist of *separated* classes. Taking these, their sums two, three, four, &c. together, and the class z, we have a collection of 2^n classes, which may be called a *full* set, and may be said to be *derived* from the collection of n separated classes.* All the classes of the set are contained in a class u of the set which is the sum of the separated classes from which the full set is derived, and may be called the *universe* of the set. The class z may be called the *zero* of the set. The whole system of classes involved in any inquiry is a system of 2^m classes where m is the number of separated classes, the product of each two of these being the non-existent class Z. In discussing a system of classes we have under consideration a number of full sets with their accompanying universes and zero classes.

364. If a be any class of a full set of which u is the universe and z the zero class, we have

$$a+u=u \text{ and } au=a$$
$$a+z=a \text{ and } az=z$$

---

* A more general meaning is given to the expression "full set" in sec. 381, and it must not therefore be assumed that conversely every full set can be derived in the manner just indicated.

and a is accompanied by a class $\bar{a}$ such that

$$a+\bar{a}=u$$
$$a\bar{a}=z.$$

Also we have

$$\overline{(a+b+c+d+\dots)}=\bar{a}\,\bar{b}\,\bar{c}\,\bar{d}\dots$$
$$\overline{(abcd\dots)}=\bar{a}+\bar{b}+\bar{c}+\bar{d}+\dots$$

where a, b, c, d, . . . are any classes of the full set. Thus the relations of the component classes of a full set are similar to those of the component classes of a whole system. The class $\bar{a}$ may be called the "*obverse of a in the full set.*" It is not of course the true obverse of a, *i.e.*, is not a', unless the full set is the whole system.

365. Any collection of n classes a, b, c, d, . . . which are such that they and their various sums and products are all different classes may be said to be a collection of *unrestricted* classes. The minimum full set of which a collection of n unrestricted classes is a component contains 2^{2^n} classes; for the separated classes of such full set are $abcd\dots$, $a'bcd\dots$, $a'b'cd\dots$, $a'bc'd\dots$, $a'b'c'd\dots$, $a'b'c'd'\dots$, &c., which are 2^n in number. This full set may be said to be *derived* from the collection of n unrestricted classes.

366. If a, b, c, d, . . . be any collection of unrestricted classes, we can always find a class λ of the derived full set, such that the classes λa, λb, λc, λd, . . . have any desired class relations to each other.*

367. Thus if we have a collection of 2^n unrestricted classes a, b, c, d, . . . , there will be a class λ such that λa, λb, λc, λd, . . . constitute a full set, and another class μ such that μa, μb, μc, μd, . . . are a collection of separated classes.

368. Suppose we have under consideration a full set T of 2^n classes. We may, if we please, ignore the relations of inclusion, &c., which they have to each other, and treating them as a collection of separated classes constitute a derived full set P of 2^{2^n} classes containing them, their aggregates, and a zero class. Here the units of T are the products τa, τb, τc, τd, . . . of a class τ and a collection a, b, c, d, . . . of 2^n unrestricted classes. When we ignore the relations of inclusion, &c., which τa, τb, τc, τd, . . . have to each other, we no longer deal with τa, τb, τc, τd, . . . but with a collection πa, πb, πc, πd, . . . of separated classes.

369. The obverse in T (sec. 364) of any class τa is $\tau a'$, the class containing all classes of T which have only the zero class in common with τa. The obverse in P of πa is $\pi a'$, the class which contains all the separated classes πb, πc, πd, . . . ; viz., all those classes arrived at by ignoring the relations of inclusion, &c., of τb, τc, τd, . . .

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* Thus Mr. VENN in his 'Symbolic Logic,' at chap. v., employs intersecting ellipses to represent unrestricted classes. He then regards parts of these as eliminated, and so makes the ellipses represent classes having any desired relations. Here λ represents the class composed of the uneliminated spaces.

370. When any collection ξa, ξb, ξc, ξd, . . . of classes of a full set T have certain relations of inclusion, &c., to each other; instead of saying that ξa, ξb, ξc, ξd, . . . have these relations, we may say that a, b, c, d, . . . have the relations "in ξ." A class ξ may be completely defined by stating that it is the most extensive class in which certain relations hold between other classes. Thus the class $\bar{a}+b$ of a full set in which a and b are unrestricted is fully defined by saying that it is the most extensive class of the set in which "all a is b," or in which $ab=a$. Further, instead of using this definition, we may simply employ the equation $ab=a$ without other words; it will then assert that the class $\bar{a}+b$ is that under consideration and will be a mark or term denoting that class. The equation $a=u$ will be a term denoting the class a of the set.

371. We might use $ab=a$ to denote, not the class $\bar{a}+b$, but the class which contains all those classes arrived at by ignoring the relations of inclusion, &c., between $\bar{a}+b$ and the various classes contained in $\bar{a}+b$.* It is in this sense that such a mark is usually employed.

372. Taking $ab=a$ as used in the last paragraph, the term $ab\neq a$, *i.e.*, "some a only is b," will represent the class arrived at by ignoring the relations of inclusion, &c., between all those classes of T which are not included in $ab=a$. Here $ab\neq a$ is the obverse of $ab=a$ in P the full set derived from the full set T by regarding the classes of the latter as separated.

373. Terms such as $ab=a$, $ab\neq a$, are called *propositions*. The difference between propositions and other terms is accidental and not essential matter of exact thought; propositions, like other terms, merely denote classes.

374. When we consider a full set T of 2^m classes τa, τb, τc, τd, . . . , and the related propositional classes, we consider a system S of 2^{2^m} classes, viz., that derived from the 2^m unrestricted classes a, b, c, d, . . . ; the classes τ and π being other classes of S. If as is generally the case T is regarded as derived from n unrestricted classes, represented by single letters A, B, C, D, . . . , the number of classes in T will be 2^{2^n}, in P will be $2^{2^{2^n}}$, in S will be $2^{2^{2^{2^n}}}$.

375. In a syllogism we have two classes called the *premisses*, *e.g.*, (1) ($ab=a$), (2) ($bc=b$). We consider the class which is the product of these, viz., ($ab=a$) ($bc=b$), *i.e.*, that which contains all the separated classes of T, which both (1) and (2) do. This class includes some classes, is included in others, &c. It is included in ($ac=a$). The syllogism indicates this fact, the class ($ac=a$) being called the *conclusion*.

376. We have then under discussion in an investigation of classes a system of 2^m units consisting of

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* If the proposition "all a is b" is taken to imply the existence of its subject a, we must exclude the zero class of T. Similarly in the case of the proposition "some a only is b" (sec. 372).

(0) a class Z,

(1) m separated classes each containing Z,

(2) $\frac{m(m-1)}{2}$ classes each containing two separated classes,

. . . .

(r) $\frac{\underline{|m}}{\underline{|m-r}\,\underline{|r}}$ classes each containing r separated classes,

. . . .

(m) a class U containing all the separated classes.

Each class of the collection (r) may be derived by adding to some class s of the collection ($r-1$) a class of (1) not contained in s.

377. We have apparently as an essential accompaniment of the idea of classes the notion of the inclusion of one class in another. Inclusion is usually regarded as a relation between *two* classes. This is not, however, really so. The notion of inclusion essentially involves that of a chain of classes with two terminals, viz., a class U which contains all classes, and a class Z which is contained in all classes, of the chain. In dealing with a class A we really deal also with the classes U and Z; and in dealing with two classes A and B we deal with the four classes A, B, U, Z. When this fact is recognised, inclusion, as commonly conceived, is seen to be a relation which, as far as the processes of exact thought are concerned, is accidental; that which is essential in it depending upon the places occupied in a system of classes by two classes relatively to two others (sec. 388).

378. The classes U and Z are not, apart from accidents, distinguished from any other classes. The system of which the units are classes is a single one. The reason why U and Z seem to hold exceptional positions is that when we discuss classes we consider their positions with reference to U and Z, which, being constantly under consideration, acquire an accidental importance.

379. There are two distinct sorts of inclusion, viz., *direct* and *indirect*. If a is contained in b, and b in c, then the inclusion of a in c may be said to be *indirect;* if a is contained in c, and there is no class b under consideration such that a is contained in b and b in c, then the inclusion of a in c may be said to be *direct*. The two classes a and c may in the latter case be said to be *adjacent*, in the former *non-adjacent*. The relations of adjacency and non-adjacency are relations between *two* classes, and do not depend upon the consideration of the classes U and Z. In a system of 2^m classes every class is adjacent to m classes. Thus in the case of the collections of sec. 376 every class of the collection (r) is adjacent to r classes of the collection ($r-1$) and $m-r$ of the collection ($r+1$).

380. The form of a system of 2^m classes is completely defined by the division of the pairs of classes into adjacent and non-adjacent pairs. It may therefore be graphically

represented by 2^m graphical units, of which pairs representing pairs of adjacent classes are linked, and pairs representing pairs of non-adjacent classes are not linked.

381. A convenient mode of building up a graphical representation of such a system is the following:—Suppose we have a graphical representation of any collection of units, say a *diagram*. To this we can add a precisely similar diagram, say we can *repeat* the diagram. The two diagrams will correspond unit to unit in one or more ways. Taking one of these ways only, we can link each graphical unit of one diagram to the corresponding unit of the other, say we can *connect* the two diagrams. Now draw a single graphical unit, repeat it, and connect the two diagrams (fig. 69). Repeat the resulting diagram and connect the two diagrams (fig. 70). Repeat the resulting diagram and connect the two diagrams (fig. 71). Repeat the resulting diagram and connect the two diagrams (fig. 72). This process can be carried on indefinitely, the number of units being each time doubled, so that the number of units after n processes is 2^n.

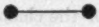
Fig. 69.

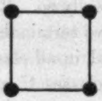
Fig. 70.

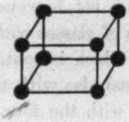
Fig. 71.

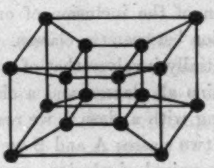
Fig. 72.

382. Each of the diagrams may be said to represent a *full set* of the whole system finally arrived at. There are of course other full sets besides these in the system. Thus in fig. 72 there are 8 full sets represented, such as that in fig. 71; and generally in any system of 2^m units there are $2m$ full sets of 2^{m-1} units.

383. We can pass from one graphical unit to another along links. We can do this by passing along a minimum number of links, or by more circuitous routes. The number of links passed over in the case in which we pass over a minimum number may be termed the *distance* between the two units. Adjacent units are at a distance 1 apart.

384. In the following sections it is to be understood that when chains connecting two units are spoken of, those containing the same number of links as the two units are distant apart are referred to. We can, of course, by zigzagging about, make the chains much longer, but such chains are not those considered, which are only the chains of minimum length.

385. Let σ_0 be any unit of a class system of 2^m units. There are m units linked to σ_0, composing a collection which may be called σ_1, every unit of which is at a distance 1 from σ_0. We have also a collection σ_2 of $\frac{m(m-1)}{2}$ units other than σ_0 and σ_1, each of the units of which is at a distance 2 from σ_0. So, generally, we have

a collection σ_r of $\frac{\underline{|m}}{\underline{|r}\,\underline{|m-r}}$ units, each of which is at a distance r from σ_0. When $r=m$ we get a single unit σ_m which is the obverse of σ_0, and is unique with respect to σ_0, being the only unit of the system which is so. The units of any collection σ_r are each linked to m units of σ_{r-1} and to $m-r$ of σ_{r+1}, but to no other units of the system, so that none of them are linked to each other. We see here that the relation of a class σ_0 to its obverse σ_m is one not depending on the relations of σ_0 and σ_m to U and Z, though expressible in terms of such relations.

386. Consider now two collections of chains of links, (1) consisting of chains from σ_0 to a unit α, (2) consisting of chains from σ_0 to a unit β (see sec. 384). There are some graphical units through which chains of both collections pass. If we classify these according to their distances from σ_0, we find that the number in each class is always greater than 1, except in the case of the greatest distance, when there is one only, which is therefore unique with respect to σ_0, α, β. If the chain from σ_0 to α passes through β, it is clear that the unit is β itself. In the same way, if we take any number of units $\alpha, \beta, \gamma, \delta, \ldots$, there is a unit unique with respect to $\sigma_0, \alpha, \beta, \gamma, \delta$, which may be one of the units $\alpha, \beta, \gamma, \delta, \ldots$ We may obtain a like unit unique with respect to $\sigma_m, \alpha, \beta, \gamma, \delta, \ldots$ We may term the unit in the former case the product of $\alpha, \beta, \gamma, \delta, \ldots$ with respect to σ_0; and in the latter case the product with respect to σ_m.

387. If σ_0 be Z, then the product of any units with reference to σ_0 will be what has been spoken of in sec. 360, simply as the *product* of the classes represented by those units. The product with respect to σ_m, which will be U, will in such case be that which was defined in sec. 360 as the *sum* of the classes.

388. If a chain from U to Z passes through two units α and β, first through α and then through β, then α and β represent classes which are such that α contains β. If no chain from U to Z passes through both α and β, then neither class is contained in the other. This makes it clear that the relation of inclusion is one in essentials depending merely on the form of a system of classes, and the position two units occupy in it relatively to two others (U and Z); or rather, as U and Z are unique with respect to each other, to one other, viz., either U or Z.

389. Suppose we have a system S containing the n unrestricted classes $a, b, c, d, \ldots$, the obverses U and Z, and the collection C of separated classes $abcd\ldots$, $a'bcd\ldots$, $ab'c'd\ldots$, &c. Here C has the same self-correspondences as a single heap. Now, if we confine our attention to those self-correspondences of S in which the collection of $2n$ units consisting of $a, b, c, d, \ldots$, and their obverses is self-correspondent, the collection C will have those self-correspondences only which are characteristic of a full set; and will not have any correspondences with other collections; also the other units of S (except Z) which may then be regarded as aggregates of the units of C taken two, three, &c., together will correspond only if they are aggregates of component collections of C which correspond; *i.e.*, they and C will have correspondences as if they

composed as many systems as there are *types* of component collections of a full set of 2^n classes.

390. If $n=4$, so that C has 16 component units, the number of these types will be 397, so that a class system containing 16 classes has 397 different sorts of component collections.* It must be noted that it is distinguished *collections*, and not distinguished *aspects* of collections, with which we are here dealing.

391. The number of types in a system of 4 units is 5. In one of 8 units it is 21. In both cases components containing all units of the systems are included.

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* See Professor CLIFFORD "On the Types of Compound Statement involving Four Classes," in the 'Proceedings of the Manchester Philosophical Society,' vol. vi., Third Series. In this paper Professor CLIFFORD denotes the 2^{16} classes of a system derived from four unrestricted classes A, B, C, D, by statements or propositions. He regards the classes A, B, C, D, and their obverses *a*, *b*, *c*, *d*, as distinguished from all other classes of the system, and thus regards the separated classes as constituting a full system, and consequently gets the division of all the classes into 396 sorts, not including the aggregate of all the classes. In the view taken in this memoir, the 2^{16} classes should all be regarded as undistinguished from each other, the distinction raised between the classes A, B, C, D, *a*, *b*, *c*, *d*, and others, being due to the accident of particular classes being selected to be denoted by single letters, and not to any essential differences. This does not, of course, affect the conclusion that the number of distinct types of component collections of a system of 16 classes is, if we do not include the collection which is the aggregate of all the classes, 396, or if we do include such collection, 397.

II. *On Evaporation and Dissociation.*—Part I.

By Professor **William Ramsay**, *Ph.D., and* **Sydney Young**, *D.Sc., Lecturer and Demonstrator of Chemistry in University College, Bristol.*

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[Plates 1, 2.]

§ 1. The phenomena exhibited by gases when exposed to varying temperatures and pressures have been shown by many eminent observers to be explicable by an extension to molecules of the laws of motion of matter which are known to be true in the case of large bodies. Such molecules of gas are supposed to be in a state of very rapid motion, the free path of each molecule bearing a very large ratio to the diameter of the molecule. As a liquid is formed by the condensation of a gas, it is clear that its molecules are in closer proximity to each other, and that the average free path of each molecule in the liquid state cannot be nearly so great as in the gaseous state. It was pointed out by **Naumann** (Ann. d. Chem. u. Pharm., 1870, 155, 325; see also **Ramsay**, Proc. Roy. Soc., 1880, April 22 and December 16) that it is conceivable that an explanation of the closer proximity of molecules in a liquid than in a gas may be that two or more gaseous molecules have united to form complex molecular groups, analogous to those complex molecules which are known as chemical compounds, in which two or more elements exist in combination.

On the other hand, it is held by some that the difference between gas and liquid is due solely to the greater proximity of the molecules in the liquid state, by reason of which they come within the sphere of mutual attraction, but do not necessarily coalesce to form groups of molecules analogous to the group of atoms in the molecule of a compound.

These views also apply to the molecular constitution of solids; it is generally held that solids differ from liquids only in the arrangement and restrained motion of their molecules.

§ 2. In support of the first view the following points have been urged:—

(*a.*) The rotation of the plane of polarised light is supposed to point to molecular grouping in liquids and solids, which does not exist in gases.

(*b.*) The existence of allotropic forms of elements, and of isomorphous forms of compounds, and the fact that heat is evolved or absorbed during passage from the one form to the other.

(*c.*) The abnormal vapour-density of sulphur and selenium among elements, and of the compound nitric peroxide appear to be undoubtedly due to the existence of complex molecules. It is to be remarked that in these cases molecular grouping occurs before the liquid condition is attained.

(*d.*) The abnormal vapour-densities of all substances at temperatures near their boiling-points, shown especially by acetic and homologous acids. Here also the grouping, if any, must occur in the gaseous state.

§ 3. The phenomena stated in (*a*) and (*b*) are explained equally well, it may be remarked, by a systematic arrangement of gaseous molecules, and do not necessarily imply union of those molecules to form more complex molecular groups; while as regards (*d*) it appears almost certain that the abnormality common to non-dissociable vapours near their condensing-points at high temperatures and corresponding high pressures, is due simply to a deviation from AVOGADRO'S law, for it disappears, at least in the case of alcohol, on lowering temperature and pressure, so as to keep the vapour nearly saturated. With acetic acid vapour, on the contrary, the abnormality, which is considerable at the ordinary boiling-point, increases greatly with reduction of temperature and pressure. It might be expected that a decrease of temperature would tend towards the formation of complex molecular groups; while it is difficult to imagine a rise of temperature, even if accompanied by a rise of pressure, bringing about this result.

§ 4. If it be true that liquids consist of more complex molecular groups than gases, that each such complex molecule is composed of a definite number of gaseous molecules, and that the molecule of a liquid may be regarded as a chemical compound of *like* gaseous molecules, then the phenomena attending the change from the solid or liquid to the gaseous state should be similar both with stable and dissociable bodies.

§ 5. Certain analogies are evident on first inspection.

(1.) To convert a liquid into gas, work must be done

(*a.*) in overcoming molecular cohesion;

(*b.*) in expansion against pressure, which may be that of the atmosphere.

If liquids consist simply of gaseous molecules in such proximity that they exercise mutual attraction on each other, the work is wholly expended in these two directions; if, on the contrary, molecules of a liquid are more complex than those of its gas, work is also done

(*c.*) in decomposing the complex molecules;

(*d.*) in imparting increased velocity to the resulting gaseous molecules.

The last assertion (*d*) will hold if the mean energy of each of the liquid molecules is equal to the mean energy of each of the gaseous molecules in contact with it. It is known, at any rate, that no heat change occurs when a saturated vapour is brought in contact with its liquid at the same temperature and pressure. Since the energy of any molecule is proportional to its mass, and to the square of its velocity, and since the mean energy of one of the complex molecules is equal to the mean energy of a single gaseous molecule, it follows that the square of the velocity of the complex molecule is $\frac{1}{n}$th of that of the gaseous molecule, where n represents the number of gaseous molecules condensed to form a complex molecule. It follows, then, that after the complex molecule has been resolved into its constituent simpler molecules, heat must be imparted to each of the latter to increase its velocity, until the energy, $\frac{1}{2} MV^2$, becomes equal to that of the remaining molecules. (See NAUMANN, 'Thermochemie,' p. 93, ed. 1882).*

(*e*.) If molecules, in becoming gaseous, acquire increased volocity, it is obvious that owing to their collision, the motion of the atoms in the molecule is also increased, a certain proportion of energy being absorbed.

Supposing the existence in liquids of complex molecular groups, the analogy is evident between the evaporation of a liquid and the vaporization of such a compound as is stable when solid or liquid, but dissociates partly or completely when gasified. In the first case the simple molecules are like each other; in the second, generally unlike.

§ 6. (2.) The density of gases is found in some cases to increase as the temperature falls to the condensing-point. This may be explained by assuming the existence of complex gaseous molecules (PLAYFAIR and WANKLYN, Trans. R.S., Edin., xxii. (3), 441; 'Annalen,' 122, 245; also NAUMANN, 'Annalen,' 155, 325); or it may be viewed, as before stated, as caused by greater molecular proximity, when mutual attraction comes into play. Similarly with those substances in which dissociation takes place in the gaseous state, the density of the mixture of gases increases with fall of temperature; and this is doubtless caused by the increase in number of complex molecules. (As regards this statement, see § 3.)

§ 7. Solids and liquids, when confined in a closed space, give off from their surfaces gaseous molecules, until there exists in that space a certain number. These gaseous molecules are termed collectively, a *saturated vapour*. After this limit, conditioned by the temperature of the liquid and gas, is reached, evaporation is balanced by condensation; the pressure exerted by the vapour is termed the *vapour-pressure* (vapour-tension) of the substance. Similarly, substances which are known to dissociate, when confined in a limited space, give off vapour, or a mixture of vapours, the molecules of which are wholly, or in part, simpler than those forming the solid or liquid. Such a vapour, or mixture of vapours exerts a pressure conditioned by the temperature. This pressure has been termed the *pressure* (or tension) *of dissociation*. As in the case of bodies that do not dissociate into unlike molecules, the pressure is dependent on the temperature, and at a given temperature it reaches a maximum, owing to equilibrium being established between dissociation and recombination, as well as between evaporation and condensation, if the latter occurs. We have already shown ('Transactions,' Part I., 1884, p. 37) that in the case of solids, where unlike molecules are not formed when change to a gaseous condition occurs, the curve which represents the maximum pressure attainable by the vapour of a solid at different temperatures represents also the maximum temperature to which the solid can be heated under different pressures, when there is free surface for evaporation. This has long been known to hold for liquids. If the work done in dissociating complex molecules of a solid or liquid into unlike simpler gaseous molecules is analogous to that expended in converting a stable solid or liquid into gas, it seems not unnatural to expect that the above relation between temperature and pressure should hold good for such bodies as dissociate in passing from the solid or liquid into the gaseous state.

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* Exception may be taken to the above statement on the ground that it is yet unknown to what the energy of a liquid is due; and that the relation between energy and temperature, with liquids, has not been ascertained.

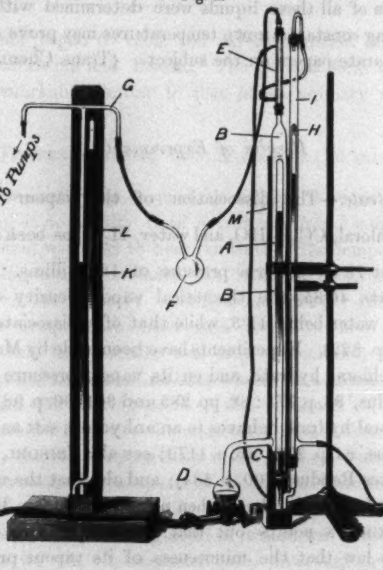
In the present memoir, the relations between temperature and pressure in the case of dissociating substances will be studied.

Description of General Methods.

§ 8. *Temperature of Volatilization under different Pressures.*—The method employed has already been described in the 'Transactions,' Part II., 1884, p. 461. It was often found more convenient to heat the substance in the still, by means of a vapour-jacket instead of a paraffin or sulphuric-acid bath. Care must be taken that the temperature of the vapour is at least 30° to 40° higher than that registered by the thermometer. For high temperatures, the vapour of aniline, methyl-salicylate, bromonaphthalene, or mercury was used as a jacket; and for very high temperatures, it was preferable to use a still with a short tube, with the stem of the thermometer outside of the apparatus. This, of course, necessitated a somewhat troublesome correction, in order to ascertain the true temperature; for different parts of the stem of the thermometer were heated to different temperatures. In many cases, air was introduced into the previously calibrated thermometer to prevent sublimation of mercury in the stem. Although the results are uniformly given in arithmetical order, yet readings were taken sometimes after raising, sometimes after lowering the pressure.

§ 9. *Vapour-pressure* (*Pressure of Dissociation*) *at different Temperatures.*—The customary method was employed of introducing the substance into a barometer-tube, heating the tube, and comparing the height of the column of mercury with that in a barometer placed in the same trough. The methods of introducing liquids or solids into the experimental tube, so as to exclude air and moisture, have been already described in the memoir referred to above. As it was necessary to heat the experimental tube to any desired temperature, and to maintain that temperature constant for any length of time, the following method was resorted to as the only practicable one. The experimental tube A was surrounded with a jacket B, and passed through an indiarubber cork, inserted into the lower opening of the jacket. In order to prevent this cork from being attacked by the hot condensed liquid, it was covered with a layer of mercury C. (It may be remarked here that it was found that the slight volatilization of this mercury did not affect the temperature, even at a temperature of 280°, with bromonaphthalene as a jacket, owing probably to the constant presence of a layer of liquid on its surface.) The pure liquid, the vapour of which served to heat the experimental tube, was boiled in a bulb, D, fused on to the side of the jacket. A narrow tube was fused on to the top of the jacket, and was surrounded by a short condenser, E. On issuing from the condenser, the upper extremity of the narrow tube was coupled, by means of lead tubing, with a reservoir, F, the object of which was to collect any liquid which might accidentally pass the condenser. A second lead tube joined F with the gauge G, and the gauge was connected with a Carre's air-pump, as well as with a Sprengel pump, a large reservoir being interposed in order to ensure constancy of pressure. A barometer, H, stood in the same trough as the experimental tube A, and was surrounded by a jacket of water of known temperature, I. On account of the gradual escape of air from the glass into the vacuous space, the barometer was boiled out from time to time. Another barometer,

Fig. 1.



K, stood in the same trough as the gauge G. The heights of the mercury were read in both cases by means of the two scales L and M, graduated on plate-glass mirror; parallax in reading was thus avoided. By means of this arrangement, the pressure in the jacket could be maintained constant for hours together, thus ensuring a constant temperature. In order to obtain any desired temperature between that of the atmosphere and 360°, the following liquids were used:—alcohol, chlorobenzene, bromobenzene, aniline, methyl-salicylate, bromonaphthalene, and mercury. These liquids have the advantage of being very stable, and of being easily obtained in large quantity in a nearly pure state, and at a low price.

The vapour-pressures of all these liquids were determined with great care; and as this method of obtaining constant known temperatures may prove serviceable to others, we have published separate papers on the subject. (Trans. Chem. Soc., 47, p. 640 and 49, p. 37.)

Results of Experiments.

§ 10. *Chloral Hydrate.*—The dissociation of the vapour of chloral hydrate $CCl_3.CH\left\}\begin{matrix}OH\\OH\end{matrix}\right.$, into chloral, $CCl_3.CHO$, and water, H_2O, has been shown by **Naumann** to be complete even at 78·5°, under a pressure of 162 millims. The vapour-density determined by him was 40·85, the theoretical vapour-density of a mixture of the vapours of chloral and water being 41·3, while that of undissociated chloral hydrate is 82·6 ('Berichte,' 1876, p. 822). Experiments have been made by **Moitessier** and **Engel** on the distillation of chloral hydrate, and on its vapour-pressure under different conditions ('Comptes Rendus,' 86, p. 971; 88, pp. 285 and 861; 90, p. 98). **Würtz** has shown that the vapour of chloral hydrate behaves to an anhydrous salt as though it contained water ('Comptes Rendus,' 84, p. 977; 86, p. 1170; see also **Friedel**, Bull. Soc. Chim., 43, p. 56; **Troost**, 'Comptes Rendus,' 100, p. 834); and also that the vapours of anhydrous chloral and of water do not evolve heat when mixed ('Comptes Rendus,' 89, pp. 190, 337, 429, 1063). **Naumann** points out that the temperature of decomposition of chloral hydrate lies so low that the minuteness of its vapour-pressure probably precludes a determination of its vapour-density at that temperature ('Thermochemie,' p. 135). So long as it retains the solid state, however, it is proved by its physical properties to be a compound. It was, therefore, deemed specially important to determine whether the curve representing its pressures of dissociation was identical with that exhibiting its volatilizing points under different pressures.

§ 11. PRESSURES of Dissociation of Chloral hydrate in Barometer-tube.

Temperature.	Pressure.	Time required for equilibrium.
°	millims.	
12·7	6·8	After standing over night.
27·9	19·0	34′
39·9	35·8	20′
50·8	72·0	24
56·1	96·2	Constant at once.
63·3	146·4	,, ,,
78·2	318·3	,, ,,

The chloral hydrate began to melt and partly liquefied at 50·8°. These results confirm those of MOITESSIER and ENGEL. The general form of the curve based on these numbers is remarkably similar to that of an ordinary vapour-pressure curve. (Plate 1.)

§ 12. TEMPERATURES of Volatilization of Chloral hydrate.

The bulb of a thermometer was covered by dipping it repeatedly in melted chloral hydrate, and allowing it to solidify until it had acquired a sufficiently thick deposit. A bath of sulphuric acid was used to heat the tube. The temperature rose gradually; the pressure remaining nearly constant. At 51·8° the substance was still perfectly solid, although above its ordinary melting-point, 50·6°; the pressure registered 11·4 millims. The temperature then rose to 57°, while the pressure rose to 12·3 millims.; after this the pressure rose only 0·1 millim., while the temperature rose to 64°. Even at 64° no sign of melting was to be noticed. The experiment was then discontinued, and the melting-point of the sublimed chloral hydrate compared with that of the portion left on the thermometer. It was found to be 50·6° for both. The substances had, therefore, apparently undergone no change on heating. It is right to observe, however, that a specimen of chloral hydrate, which had been repeatedly melted, and which was examined after two years, left on treatment with water an insoluble residue, the melting-point of which was above 130°. The melting-point of the residue on the thermometer-bulb, however, showed that it did not consist of this substance, which is possibly a polymeride.

§ 13. In the second experiment, with the temperature at 50·2°, the pressure was 7 millims.; the temperature rose to 55°, pressure rising to 7·4. It was impossible to lower the pressure further, for vapours given off by the chloral hydrate attacked the mercury of the SPRENGEL pump, forming mercurous chloride; this is a remarkable circumstance, for chloral hydrate had no perceptible action on the mercury in the barometer-tube, at a much higher temperature. After this experiment, the chloral hydrate adhering to the bulb of the thermometer was carefully examined, and it was found that the bulb was completely coated, and that the substance was in perfect contact with it. The minimum thickness was 0·8 millim., and the hydrate extended 12 millims. below the bulb and about 30 millims. above it. The hydrate was therefore undoubtedly heated above its usual melting-point without melting.

§ 14. The third experiment began with a temperature of 52° and a pressure of 9·2 millims. Air was then admitted, so as to raise the pressure to 24 millims., while the temperature was rising. The registered temperature was 53°. More air was admitted from time to time, and the following readings were taken :—

Pressures	40·3	53·0	53·0	60·6
Temperatures. . .	52·0	50·0	49·0	49·0 (melting).

As soon as the substance began to melt, air was removed by pumping. When the pressure was reduced to 40·3 millims., the temperature being 48·4°, the substance entirely solidified, and after further reduction of pressure to 23 millims., the temperature rose to 51°. Air was then admitted, so as to raise the pressure to 61·6 millims., when the hydrate melted. It is noticeable from this experiment, that admission of air, to increase the pressure, lowered the temperature, and its removal raised the temperature; and that the substance melted only when the temperature had fallen below its ordinary melting-point; and that the pressure at which fusion occurred was in this, and in other similar cases, about 60 millims.

§ 15. CONFIRMATION of the above results was obtained with a fourth series.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure	Temperature.
millims.	°	millims.	°	millims.	°
7·4	50·0	41·0	56·0	42·0	50·0
7·5	52·0	40·0	53·7	falling	53·0
7·6	54·0	47·5	53·0	,,	54·0
7·7	55·0	59·6	52·0	,,	55·0
8·1	56·0	59·6	51·0	,,	56·0
8·1	57·0	59·6	50·7	..	..
Substance solid ; air admitted.		Melting ; air removed by pumping.		Pressure increased to 64 millims. Substance melted.	

§ 16. In the fifth series, to ascertain if the chloral hydrate would melt if the pressure were high, and the temperature raised towards the melting-point, the substance was heated at a pressure of 24 millims. It began to melt when the temperature registered was 24°. It was evident that the heat had not had time to penetrate to the interior. The substance was cooled, and again heated at a pressure of 16·5 millims. The hydrate melted only when in contact with the stem of the thermometer, where it was evidently heated by conduction. These observations were confirmed by a sixth experiment, in which the pressure was 25 millims., and the temperature registered, when fusion began, 37°. After cooling and lowering the pressure to 15·2 millims., the temperature rose on again heating to 55°, without the substance melting. As these results are so very unusual, it was deemed advisable to check the experiments, showing the possibility of heating the chloral hydrate above its melting-point without its fusing; entirely similar results were obtained in two separate series of experiments.

§ 17. The general conclusion to be drawn from these experiments is, that the relations between temperature and pressure with chloral hydrate differ from those shown in the case of bodies which do not dissociate, and indeed that a fall of pressure allows of a rise of temperature, and that a rise of pressure lowers the temperature of this dissociating body. It is also to be remarked that this substance undergoes no change in composition, so long as it remains solid, while it is known that when the liquid hydrate is distilled, separation into its constituents takes place, and that the residuum has a different composition from that of the distillate (Naumann, 'Berichte,' 1879, p. 738).

§ 18. As the results of a determination of the vapour-pressures of chloral by Moitessier and Engel are meagre, it was thought worth while to determine these constants by the still-method, as chloral attacks mercury, and another cause of error is the formation of a small quantity of hydrogen chloride when chloral is heated.

VAPOUR-PRESSURE of Chloral.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
5·3	−13·0	29·6	18·0	248·6	65·2
7·5	− 6·9	37·9	22·7	296·6	69·7
8·4	− 5·0	49·8	28·2	358·3	74·8
10·3	− 1·0	61·9	32·0	415·0	79·7
12·3	+ 2·0	62·9	32·7	463·3	82·7
13·6	4·0	72·6	35·9	518·0	85·3
15·7	6·5	79·1	37·5	565·0	88·6
16·5	6·9	83·8	38·9	608·0	90·7
17·0	8·0	95·5	41·9	671·5	93·8
18·3	9·2	121·3	47·6	704·9	95·3
20·1	10·8	160·0	54·0		
21·6	12·8	200·7	59·7		

§ 19. It will be noticed from § 10 that Naumann found the vapour-density at 78·5° under a pressure of 162 millims. to point to complete dissociation. But the vapour-pressure of chloral hydrate at 78·5° is 322 millims., hence the vapour in his experiments was very far from being saturated. Since dissociation decreases with increase of pressure, it was deemed possible that at pressures nearer saturation, dissociation might not be complete. The following experiments were carried out to test this point:—

A quantity of substance was roughly weighed (about 0·016 gram.), so calculated that its vapour would exert a pressure nearly that of saturation at 60°; and its vapour-density was then determined by Hofmann's method; the tube was heated by alcohol boiling under reduced pressure.

Weight.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage of molecules decomposed.
grm.	millims.	cub. centims.			per cent.
0·01587	113·3	33·64	3811	43·08	91·74
..	107·0	36·14	3867	42·46	94·54
..	102·5	37·76	3870	42·42	94·72
The temperature was then raised to 78·2°					
..	119·6	34·58	4136	41·87	97·28

The temperature was raised to 131·8° by a jacket of chlorobenzene vapour, and two readings of pressure and volume were taken. From these the values of P.V. were respectively 4835 and 4829; as it is certain that dissociation must be complete at this temperature, the actual weight of substance was calculated from the mean value of P.V., and the number obtained was employed in the above calculation of vapour-densities. It is thus evident that at 60°, and at pressures near that of saturation, dissociation is not quite complete. In this, and in all other cases in which dissociation was nearly complete, a very long time elapsed before the whole of the substance had evaporated.

§ 20. *Butyl-chloral Hydrate,* $C_3H_4Cl_3.CH\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.—This body resembles chloral hydrate in dissociating into butyl-chloral and water. Its vapour-density has been determined by ENGEL and MOITESSIER in HOFMANN's apparatus at 160°, and found to point to complete dissociation. It is stated by these experimenters that it begins to boil at 100°, and that the water distils off, leaving butyl-chloral, boiling at 165°. Butyl-chloral hydrate was found to separate on heating into two layers, the upper of which consisted mainly of butyl-chloral. A few determinations of vapour-pressures were made by MOITESSIER and ENGEL, and the following numbers were obtained by them:—

Temperature.	Pressure.
°	millims.
16·8	18·3
46·0	62·8
65·0	125·0
78·4	331·0
100·0	Over 760.

§ 21. PRESSURES of Dissociation of Butyl-chloral hydrate in Barometer-tube.

Temperature.	Pressure.	Time required for equilibrium.
°	millims.	
15·0	5·8	2 hours
35·0	23·1	81′
16·0	9·5	Stood all night.
35·0	25·9	51′
50·0	49·5	52′
60·0	86·0	95′
70·0	189·7	73′
77·8	307·0	28′
85·0	428·0	7′
90·0	569·7	2′

The curve is represented in Plate 1.

§ 22. TEMPERATURES of Volatilization of Butyl-chloral Hydrate.

The thermometer-bulb was coated as usual, and the still was jacketed with aniline vapour. The initial pressure was 2·15 millims. The temperature rose gradually to 68·5°, and then fell again to 66·5°; the pressure falling to 2·0 millims. The pressure was then raised to 6·8 millims.; the temperature continued to fall very slowly to 66°. On raising pressure to 15·2 millims., temperature fell to 65·5°; and with a pressure of 28·5 millims. temperature remained constant. When pressure was raised to 52·7 millims. temperature rose to 66°; pressure was increased to 65·9 millims., when temperature rose gradually to 69·7°, when the substance in contact with the stem of the thermometer became moist. On reducing pressure to 21·8 millims. solidification immediately ensued; but as the substance had largely evaporated, readings of temperature were doubtful.

A second series of experiments was made. The initial pressure was 1·9 millims., the temperature rising to about 63°. On raising pressure to 3·8 millims., no alteration in temperature was noticed. At 26·1 millims. temperature rose slowly to 64·5°. Pressure was then reduced to 13·9 millims., and the temperature fell to 63°. The reduction of pressure was continued until it reached 2·8 millims.; the temperature fell to 62·5° when the pressure was 5·5 millims., and gradually rose again to 64°. Pressure was then raised to 48 millims., and temperature rose to 68°. With rise of pressure to 65·2 millims., temperature rose to 69·2°, and the upper portion of the substance melted. On reducing pressure to 22 millims. solidification occurred, and temperature fell to 65·4°.

§ 23. It will be seen that these results are most erratic; but it is to be noted that the total range of temperature was only from 62·5° to 69·2°, while the pressure varied from 1·9 millims. to 65·9 millims. The only conclusion to be drawn is that temperature and pressure are independent of each other.

§ 24. *Chloral methyl-alcoholate*, $CCl_3CH\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$.—This substance is formed by direct combination of chloral and methyl alcohol, with evolution of a large amount of heat. It has been little investigated. Its boiling-point is given by **Martins** and **Mendelssohn-Bartholdy** at 98° ('Berichte,' III., p. 443), and by **Jacobsen** at 106° ('Annalen,' 157, p. 243). The melting-point is stated by **Jacobsen** to be 50°. We find it, however, to be 40·2°. These numbers are discordant, but it is to be noticed that the numbers given by **Jacobsen** are with methyl and ethyl compounds of chloral invariably 8° to 10° higher than those given by other observers.

The methyl alcohol used by us in preparing this body was made from pure crystals of methyl oxalate, and was carefully dried. It was mixed with chloral, and the resulting compound was crystallized over sulphuric acid. The crystallization of both ethyl and methyl compounds, from their solution in the respective alcohols, is extremely beautiful. The crystals grow upwards out of the liquid, and assume the form of luxuriant vegetation.

§ 25. **Pressures** of Dissociation of Chloral methyl-alcoholate in Barometer-tube.

Temperature.	Pressure.	Time required to establish equilibrium.	Remarks.
°	millims.		
17·0	8·8	1 h.	Solid.
35·0	17·0	16′	,,
40·0	18·1	Constant at once.	,,
45·0	21·3	15′	Liquid.
40·0	14·9	35′	Liquid, cooled below M.P.
35·0	10·3	50′	,, ,, ,,
50·0	30·7	8′	Liquid.
55·0	40·0	5′	,,
60·0	56·6	2′	,,
65·0	73·2	4′	,,
70·0	98·5	5′	,,
78·05	154·2	3′	,,

The level of the mercury in the trough was then raised, and the tube allowed to cool; complete condensation occurred, and after 16 h. the mercury was in complete contact with the solid at the top of the tube. The level was then lowered.

Temperature.	Pressure.	Time required to establish equilibrium.	Remarks.
°	millims.		
18·0	9·3	48′	Solid.
85·0	218·9	12′	Liquid.
90·0	281·4	19′	,,
95·0	358·4	7′	,,
100·0	452·8	6′	,,
105·0	566·2	26′	,,

It will be noticed that the liquid has apparently a lower vapour-pressure than the solid. At 35° the vapour-pressure of the solid is 17 millims., and of the liquid only

10·3 millims. Now, as we have already shown, that with stable substances the solid has invariably a lower vapour-pressure than the liquid ('Transactions,' Part II., 1884, p. 461), and as from theoretical considerations this must be so; and as it is also evident that the melting of chloral methyl-alcoholate must be accompanied by absorption of heat, for when the liquid substance is allowed to cool below its solidifying point, temperature rises when solidification begins; it appears to us necessary to account for this phenomenon by the supposition that the products of dissociation are soluble in the liquid, and are therefore prevented from exerting their full pressure. Similar phenomena have been observed with the ethyl alcoholate, and it was noticed that when liquefaction commenced pressure fell at once. (The curve is given in Plate 1.)

§ 26. TEMPERATURES of Volatilization of Chloral methyl-alcoholate.

The initial pressure in the still was 2·2 millims. On heating with aniline vapour, the temperature gradually rose more and more slowly to 40·6° without alteration of pressure. On raising pressure to 5·5 millims., the substance melted completely at once. The melting pressure lies, therefore, between 2·2 and 5·5 millims. Here, again, no relation between temperature and pressure is observable.

§ 27. It was noticed that the vapour-pressure of the methyl alcoholate in the barometer-tube was lower than that of the hydrate at the same temperatures, in spite of the fact that methyl alcohol is more volatile than water; and it appeared likely that the substance would be more stable than the hydrate. This was found to be the case by the following determinations of vapour-density. It will be noticed that while the vapour-pressure at 78·5° is 160 millims., the density was determined at 131·4 millims.

VAPOUR-DENSITIES of Chloral methyl-alcoholate.

Weight.	Temperature.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage number of molecules decomposed.
	°	millims.	cub. centims.			per cent.
0·0203	78·5	131·4	33·53	4406	50·32	78·06
—	„	117·0	38·03	4450	49·82	79·84
—	132·1	148·6	38·01	5648	45·24	100·0
—	„	134·7	42·28	5695	44·86	„
—	„	150·9	37·58	5671	45·06	„

The theoretical vapour-density of the dissociated substance is 44·8.

§ 28. *Chloral ethyl-alcoholate*, $CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right.$.—Formed by direct combination of anhydrous chloral with ethyl alcohol. It was crystallized from its solution in ethyl alcohol. It is stated by JACOBSEN to melt at 56° (*loc. cit.*); by LIEBEN at 46° ('Berichte,' III., p. 909; and we find its melting-point to be 46·5°. The boiling-point is given by **Lieben** as 115°. Its vapour-density has been determined by **Lieben**, and found by **Dumas**'s method to be 53·12 at 157°, and 50·38 at 198°. **Würtz** has also determined the vapour-density by **Hofmann**'s method, and found at 100°, with a pressure of 247·6 millims., the vapour density to be 48·07. The theoretical density of the mixture of chloral and alcohol is 48·3. By **Dumas**'s method the alcoholate would be submitted to fractional distillation, which would entail a residue containing excess of chloral; and it is more likely that the higher vapour-density obtained by **Lieben** is to be ascribed to this cause than to incomplete dissociation.

§ 29. VAPOUR-PRESSURES of Chloral ethyl-alcoholate in Barometer-tube.

Series I.

Temperature.	Pressure.	Time.	Remarks.
°	millims.		
14·0	13·5	2 days	Solid.
35·0	24·4	22′	"
45·0	23·1	13′	Trace of liquid showing.
50·0	24·7	22′	Liquid.
55·0	34·6	5′	"
60·0	46·6	9′	"
65·0	62·7	3′	"
70·0	84·0	5′	"
75·0	111·8	3′	"
78·0	130·0	3′	"
Cooled to 50·0	24·7	45′	Recombination.
" 35·0	9·8	23′	Still falling; liquid, cooled below solidifying point.
12·0	11·2	18 hours	Solid.
35·0	24·3	19′	"
85·0	187·3	31′	Liquid.
90·0	242·2	15′	"
95·0	308·8	5′	"
100·0	387·8	10′	"
105·0	487·7	10′	"
109·4	585·4	9′	"

§ 30. Series II.

Temperature.	Pressure.	Time.	Remarks.
°	millims.		
15·0	9·1	1 hour	Solid.
35·0	22·8	19′	"
40·0	24·7	25′	"
45·0	25·1	15′	"
50·1	25·9	37′	Liquid.
60·0	47·1	12′	"
Cooled to 40·0	14·7	112′	Still liquid.
" 35·0	12·4	50′	Still liquid; pressure falling slowly.
35·0	19·9	16′	Solid.

Here, again, the pressures in the solid are higher than in the liquid state, and probably for the same reason. On referring to the curve in Plate 1 it will be noticed that that portion representing the pressure in contact with liquid below the melting-point is continuous with that above the melting-point; whereas the pressure of the vapour in contact with solid is somewhat irregular, as is also the case with the methyl compound.

§ 31. TEMPERATURES of Volatilization of Chloral ethyl-alcoholate.

Series I.—The initial pressure was 2 millims.; the temperature of the alcoholate, heated by aniline-vapour, rose more and more slowly until it reached 47·7°. The pressure was then raised to 8·1 millims., when the substance melted.

Series II.—At a pressure of 2·55 millims. the temperature rose to 47°; air was admitted so as to raise the pressure to 6·1 millims., the alcoholate at once melted, and did not re-solidify on reducing pressure to 5·1 millims. It was thus impossible to detect any relationship between temperature and pressure.

§ 32. VAPOUR-DENSITIES of Chloral ethyl-alcoholate.

Weight.	Temperature.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage number of molecules decomposed.
grm.	°	millims.	cub. centims.			per cent.
0·02066	78·35	111	38·42	4265	52·88	82·68
		117·7	36·28	4270	52·82	82·89
		122·9	34·68	4262	52·95	82·44

It is thus evident that this body is not wholly dissociated at 78·35° when the pressure bears the ratio to that of saturation of 111 or 123 to 130.

We propose to study in greater detail the dissociation of these interesting substances, as revealed by their vapour-densities; these determinations, however, suffice to show that they are capable of existing partially undissociated.

§ 33. *Ammonium Carbamate.*—The formula of pure ammonium carbamate is $CO\begin{cases}NH_2\\ONH_4\end{cases}$; but from the nature of our experiments we were compelled to use the commercial salt, the composition of which is variable.

The dissociation pressures of this substance have been very accurately determined by NAUMANN ('Berichte,' 1871, p. 782); by ISAMBERT ('Comptes Rendus,' 97, p. 1212); and by MOTESSIEIR and ENGEL ('Comptes Rendus,' 93, p. 595). As the results of all three observers agree with each other, a redetermination was unnecessary. Suffice it to say that they give a regular curve of the usual form, reproduced in Plate 1.

It is also known from numerous experiments by NAUMANN ('Annalen,' 160, p. 5, and

'Berichte,' 1871, p. 780); by BINEAU ('Annales,' 67, p. 240); and by H. ROSE (Pogg. Ann., 46, p. 363), that the vapour-density of ammonium carbamate is 13·0, corresponding to complete dissociation into $2NH_3+CO_2$. It might, therefore, be expected to yield results somewhat analogous to those obtained with chloral hydrate.

§ 34. TEMPERATURES of Volatilization of Ammonium Carbamate.

As it was impossible to coat the bulb of the thermometer in the usual way with this substance, a block of commercial carbamate was drilled with a hole, which the thermometer exactly fitted; and it was then turned in a lathe to form a cylinder of convenient size. The following numbers refer, therefore, to commercial carbamate, or, as it is usually termed, carbonate of ammonia. The apparatus was the same as that employed for chloral hydrate. To ensure thorough condensation of the evolved gases, tubes containing pumice-stone, moistened with sulphuric acid, and stick-potash were interposed between the apparatus and the pump. The jacket was the vapour of boiling aniline.

The first series consisted of two readings, every care being taken to keep the pressure low. The pressures were 5 and 9 millims. respectively, and the temperatures 62° and 64°.

The second series gave the following numbers :—

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature
millims.	°	millims.	°	millims.	°
100	65·8	145·5	64·2	130	66·0
115	65·4	162·0	67·7	210	66·0
130	64·5	156·0	68·0	202	65·4
139	63·5	144·0	67·4	200	65·0
145	63·3	130·0	66·5		

From these experiments it will appear that, as in previous cases, pressure and temperature are independent of each other. The maximum temperature attained was 68°, although the temperature of the jacket was over 180°. The results are shown in Plate 1.

§ 35. *Ammonium Chloride*, NH_4Cl.—This substance has given rise to long discussions. The solution of ammonium chloride is known to dissociate on boiling, for ammonia is first evolved, and the residual liquid is acid (FITTIG, 'Annalen,' 128, p. 189). Its vapour density corresponds to a mixture of NH_3 and HCl at 350° and atmospheric pressure (DEVILLE and TROOST, 'Comptes Rendus,' 56, p. 895), and also at higher temperatures. HORSTMANN, from not very concordant results, concluded that its vapour-density is greater at 300° and a pressure of from 40 to 60 millims., than at 360° under normal pressure ('Berichte,' 1869, p. 299). At 360° DEVILLE found that on mixing the gases heat was evolved, necessarily implying some combination; WANKLYN, however, states that combination is only partial. **Marignac** calculated the latent heat of vaporization of NH_4Cl and found it to be 706 calories; while **Favre** and **Silbermann** give the heat of combination of NH_3 and HCl as 743·5 or 715·5 calories, calculating by different methods. **Horstmann** determined the vapour-pressure by distilling the substance in an iron tube closed by a cork in which were three holes; one for a manometer, one for a thermometer, and one for exhausting air, and so lowering pressure. And from his observations, the details of which he does not record, he constructed a curve showing the relations of pressure and temperature ('Berichte,' 1869, p. 137). On referring to this curve it will be seen that his results closely agree with those obtained by us. **Than** contradicts **Deville's** results as regards rise of temperature on mixing the gases, by experiments conducted on a different principle; at 350° he found no evolution of heat, or, more correctly, noticed no contraction, while between 330° and 340° contraction occurred ('Annalen,' 131, p. 129). The well-known experiments on the diffusion of the hot vapour of ammonium chloride point to at least partial dissociation.

§ 36. Vapour-pressures of Ammonium chloride in Barometer-tube.

For temperatures between 98° and 280° an ordinary barometer-tube was used. As mercury-vapour at 280° exerts a pressure of 155·17 millims., it was first advisable to determine whether a mixture of mercury-vapour and another vapour on which it had no action could be relied on as giving the sum of their pressures.

A barometer-tube was boiled out, and jacketed with bromonaphthalene, no substance being introduced. At a pressure of 755·9 millims., and at a temperature as determined by the vapour-pressure of bromonaphthalene of 280·1° (see § 9), the vapour-pressure of mercury, after all corrections had been introduced, was found to be 158·8 millims. On cooling there was a certain amount of air present which had been given off from the walls of the barometer-tube. The pressure exerted by this air was read at 24°, and was found to be 10·6 millims. The volume occupied by this air was (23·3 millims. × by area of the tube), while at 280·1° it was (159·3 millims. × by area of tube); hence the pressure at the higher temperature was found by the equation

$$\frac{10{\cdot}6 \times 23{\cdot}3 \times 553{\cdot}1}{159{\cdot}3 \times 297} = 2{\cdot}9 \text{ millims.}$$

The vapour-pressure of mercury is therefore 158·8 − 2·9 = 155·9 millims. This is identical with that given by **Regnault**, for mercury-vapour at 280·1°.* This tube without being emptied was inverted and again boiled out *in vacuo*. Bromonaphthalene was then introduced, and the tube was jacketed with bromonaphthalene vapour, boiling under reduced pressure. The temperature was occasionally raised by increasing the pressure, and readings were taken. The results obtained were always too low, and were variable. The cause of this turned out to be the slow rate at which the mercury-vapour diffused through the layer of liquid bromonaphthalene on the surface of the mercury, for on lowering the temperature the pressure of the bromonaphthalene vapour, after the pressure of mercury-vapour had been subtracted, was found to be the same as that under which the bromonaphthalene which jacketed the tube, was boiling. The detailed results are as follows:—

---

* From our revised table of the vapour-pressures of mercury the pressure at 280·1° is 157·7 millims.

Temperature.	Pressure of bromonaphthalene in jacket.	Total pressure in barometer-tube.	Vapour-pressure of mercury.	Δ.	Corrected to 0°.
°	millims.	millims.	millims.		millims.
238·2	290·6	346·7	55·5 (54·1)*	291·2 292·6	290·1 291·5

The level of the mercury was fluctuating about 1 millim.

It is thus seen that the combined vapour-pressure of these two substances is equal to the sum of the two vapour-pressures taken separately.

§ 37. A fresh tube was boiled out, and ammonium chloride was introduced. On heating with vapours of different liquids under different pressures the following results were obtained:—

Temperature.	Pressure.	Duration of experiment.
°	millims.	
98·2	0·2	Constant
122·9	3·5	23′
132·0	3·9	10′
140·9	4·3	Constant
151·9	4·7	7′
165 9	4·9	8′
183·3	5·5	34′
200·0	9·1	36′
210·1	12·3	60′
223·0	18·1	32′
241·9	32·1	29′
251·4	48 8	43′
261·3	72·5	65′
271·1	99·4	11′
280·7	144·4	?

The last observation admitted of no regular time-curve, on account of the difficulty of forcing up the vapour. A constant result was finally obtained at the pressure given.

§ 38. After cooling, a permanent gas remained, exerting a pressure of 50·2 millims. This after two days had fallen to 44 millims. The tube was then inverted, which removed some of the gas, and after being placed in position, was again heated. The atmospheric pressure was 760 millims., hence the boiling-point of bromonaphthalene was 280·3°. The pressure now rose to 145·9 millims., almost identical with the former reading. After again cooling, the pressure was 35 millims. On introducing water, a portion, at least, of the permanent gas was dissolved. As the pressure thus obtained was identical within limits of error of experiment with that yielded by the still-

* From our table.

method, which will afterwards be given, and as this was not the case with other dissociating substances, the highest reading was repeated.

§ 39. The vapour-pressure of mercury was redetermined in the same manner as before; the tube was jacketed with bromonaphthalene at a pressure of 752·2 millims.; the temperature corresponding was 280°. The vapour-pressure was found, after the necessary corrections, to be 156 millims. After cooling, the pressure due to air was 1·7 millim.; this, corrected as before, gives a pressure of 0·6 millim. at the higher temperature. The pressure of the mercury-vapour is therefore 155·4 millims. From REGNAULT'S numbers, 155·2 is the pressure at this temperature.*

This tube, without being emptied, was boiled out again *in vacuo*, and some ammonium chloride, prepared from pure hydrochloric acid and ammonia, and previously strongly heated, was introduced with the usual precautions. The tube was again jacketed with bromonaphthalene vapour, boiling at a pressure of 755·7 millims., corresponding to the temperature 280·1°; the pressure read was 145·4 millims., a number agreeing very closely with those previously obtained, viz., 144·4 and 145·9 millims.

§ 40. When the tube cooled, a permanent gas remained, which exerted a pressure of 18·3 millims. This amounts to a pressure at the higher reading of 4·2 millims. As a very long time was allowed so as to make certain of no further rise when the ammonium chloride was heated, the presence of this gas cannot be accounted for by a gradual decomposition of the ammonia, for we have shown (Chem. Soc. J., 1884, p. 88) that ammonia begins to decompose only at about 500°, even when hydrochloric acid is absent. It might, however, be due to some extent to the action of hydrochloric acid on mercury. On inclining the tube, this gas formed a bubble of considerable size at the top. Water was then introduced, and almost complete absorption occurred. It appears certain, then, that gaseous hydrogen chloride and ammonia, when perfectly dry, combine very slowly. In any case, the error, owing to presence of permanent gas, amounted to only 4·2 millims.

§ 41. It was deemed advisable to ascertain the vapour-pressure of ammonium chloride at still higher temperatures, and for that purpose the ordinary arrangement was inadmissible. We, therefore, adopted a method, the principle of which will be seen from the accompanying diagram. A is a tube, at the closed end of which a mass of ammonium chloride was placed above the constriction at B. This was done before the tube had been bent. Mercury was then introduced, occupying the level shown. This tube was surrounded by a jacket, C, containing a little mercury; and was closed by a tight-fitting indiarubber cork, D, through which the open end of the tube, A, projected. The tube A was connected by means of lead-tubing with a differential gauge, E, behind which stood a graduated mirror scale, and with a force and exhaust-pump, G, so that pressure on the mercury in A could be increased or diminished to a known amount at will. The pressure exerted on the mercury in the closed limb of A was equal to atmospheric pressure plus or minus the difference of levels in the differential gauge, plus or minus the difference of levels in the tube A, all reduced to 0°.

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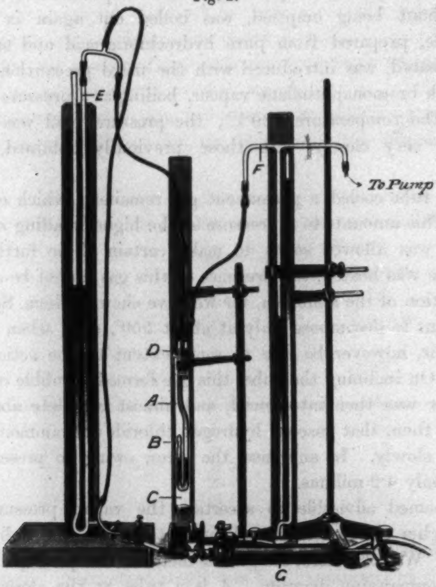
* From our revised table, 157·35 millims.

§ 42. Through a second hole in the indiarubber cork D a tube passed to a gauge, F, and from that to an exhaust-pump. The mercury in C could thus be caused to boil under any desired pressure, heating A to corresponding temperatures. For the measurement of these temperatures, REGNAULT's data for the vapour-pressures of mercury were used.

Fig. 2.



§ 43. A preliminary experiment was made in which the tube A contained only mercury, which had been repeatedly boiled out *in vacuo*. The following results were obtained :—

Pressure under which mercury boiled.	Pressure in A.	Δ.
millims.	millims.	millims.
267·6	266·7	0·9
378·3	377·0	1·3
755·0	751·8	3·2

The error in pressure is thus seen to be less than 0·5 per cent., and corresponds to an extremely minute difference in temperature; in the last instance it is barely 0·20°.

§ 44. In experiments on the vapour-pressures of ammonium chloride it was unnecessary to boil out the tube A, for it was possible to ensure absence of air by raising the pressure, heating the substance, and then reducing pressure so as to allow gas to escape. The mass of solid ammonium chloride could not pass the constriction. At a temperature of 320° it was considered certain that all air had been removed when this operation had been repeated six times, a considerable interval of time elapsing between each escape. A large number of preliminary experiments showed that the pressure rose steadily, and as this was considered at first to be due to dissociation, time-curves were constructed. In order, as we imagined, to shorten the time required, the pressure in the differential gauge was raised before each reading, so as to keep the volume of gas constant.

§ 45. For the sake of clearness the experiments are arranged in the order of temperature. At 290° vapour was allowed to escape, and a reading was immediately taken, with the following result:—

Temperature.	Pressure.
°	millims.
290	188·5
300	250·6
,,	252·5
310	342·4
,,	342·1
320	445·9
,,	443·7
330	597·6
,,	596·0

§ 46. A considerable number of experiments were made at 320° and 340°, pressure being allowed to rise.

At 320°, the following initial readings were obtained:—449·7 millims. and 447·7 millims. Having noticed that pressure steadily rose, after these readings had been taken, it was resolved to construct time-curves, so as to ascertain the rate of increase, and the final value. But it was found that this rate was sensibly constant during any one experiment, although it differed in each experiment, and was always slower after each escape of vapour. Since the explanation of the results which we propose to give was only arrived at after careful examination of these time-curves, it is necessary to give the numbers in detail. The third column will be explained later.

I. Temperature, 320°. Rate of increase of pressure, 1 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	
449·2	0	449·2	0
451·1	5	446·1	5
457·2	11	446·2	11
463·1	17	446·1	17

II. Temperature, 320°. Rate, 0·85 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	
449·3	0	449·3	0
449·1	4·2	444·9	5
456·2	9·3	446·9	11
460·2	13·6	446·6	16
462·7	16·1	446·6	19

III. Temperature, 320° (much vapour let out). Rate, 0·545 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
447·5	0	447·5	0
448·1	2·7	445·4	5
453·9	5·4	448·5	10
457·6	9·8	447·8	18
470·3	20·7	449·6	38

IV. Temperature, 320°. Rate, 0·513 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
449·7	0	449·7	0
451·7	2·6	449·1	5
457·4	10·8	446·6	21
468·1	19·0	449·1	37

V. Temperature, 320°. Rate, 0·481 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	
446·0	0	446·0	0
448·8	2·4	446·4	5
453·9	5·3	448·6	11
460·8	8·7	452·1	18
463·8	14·9	448·9	31
474·7	25·0	449·7	52
481·6	32·7	448·9	68

VI. TEMPERATURE, 320° (tube re-filled). Rate, 0·683 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
447·1	0	447·1	0
465·1	25·3	439·8	37
510·0	58·8	451·2	86
554·5	102·5	452·0	150
610·0	164·0	446·0	240
662·5	225·5	437·0	330
706·3	266·5	439·8	390

VII. TEMPERATURE, 320° (large amount of vapour allowed to escape). Rate, 0·297 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
438·4	0	438·4	0
447·1	8·9	438·2	30
458·1	26·7	431·4	90
477·5	49·0	428·5	165
517·8	78·7	438·3	265

VIII. TEMPERATURE, 320°. Rate, 0·2142 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
438·4	0	438·4	0
445·4	5·1	440·3	24
461·3	23·3	438·0	109
478·4	43·7	434·7	204
496·0	58·7	437·3	274
511·8	71·5	440·3	334

IX. TEMPERATURE, 340°. Rate, after about 20′, 0·495 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
728·1	0	728·1	0
765·7	6·4	759·3	13
784·3	17·3	767·0	35
806·6	34·6	772·0	70
813·8	52·0	761·8	105
825·2	54·4	770·8	110
838·8	71·8	767·0	145

X. TEMPERATURE, 340°. Rate, 0·385 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
684·2	0	684·2	0
748·2	2·3	745·9	6
758·6	7·3	751·3	19
774·2	20·0	754·2	52
786·9	32·7	754·2	85
793 3	44·7	748·6	116

XI. TEMPERATURE, 340°. Tube re-filled. Rate, after 20′, 1·02 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
720·7	0	720·7	0
761·8	7·1	754·7	7
780·9	20·4	760·5	20
804·0	44·9	759·1	44
827·8	68·3	759·5	67
859·2	98·9	760·3	97

XII. TEMPERATURE, 340°. Rate, after 20′, 0·372 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
730·9	0	730·9	0
755·8	1·9	753·9	5
774·7	9·3	765·4	25
787·0	23·1	763·9	62
796·3	34·2	762·1	92
810·8	45·4	765·4	122

XIII. TEMPERATURE, 340°. Rate after 20′, 0·300 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
714·4	0	714·4	0
756·3	1·2	755·1	4
769·9	6·6	763·3	22
775·0	12·6	762·4	42
782·2	20·1	762·1	67
835·8	68·4	767·4	228
886·0	123·9	762·1	413

XIV. TEMPERATURE, 340°. Rate, 0·191 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
767·4	0	767·4	0
800·3	35·1	765·2	184
805·0	40·3	764·7	211
809·0	48·9	760·1	256
839·2	77·0	762·2	403
845·9	86·5	759·4	453
857·9	95·1	762·8	498
866·9	103·3	763·6	541
870·1	110·0	760·1	576

§ 47. As in all these experiments the volume was kept nearly constant, a constant increase of pressure denotes a constant evolution of gas. This would not have been the case had the volume been allowed to increase. It seemed impossible that such results could have been produced by dissociation; and as it was believed that this constant evolution of gas was due to the action of hydrochloric acid on mercury, this supposition was put to the test. On heating mercury with ammonium chloride for three hours to 330–340° in a sealed tube, it was proved, on treating the contents with water, that mercury had entered into solution as chloride. This has also been noticed by THAN ('Annalen,' 131, p. 131). It would appear that the rate of action depends on the quantity, and therefore on the surface of the solid ammonium chloride present; for it diminished after each escape of gas. It was, therefore, possible to calculate the pressure due to the vapour of ammonium chloride or of its products of dissociation; for it may be considered certain that the rate of action of ammonium chloride on mercury during one experiment is constant. By deducting the product of the constant rate of increase of pressure into the time, from the read pressures, the true vapour-pressure, or dissociation-pressure of ammonium chloride at each time of reading could be calculated. It will be seen that at 320° the vapour-pressure is constant throughout the whole experiment; while at 340° the pressure due to ammonium chloride rises rapidly during the first twenty minutes, and then remains constant. Now, although both the initial and final pressures with different experiments at 340° differed widely from each other, yet, calculating in this way, the result varies within very small limits. We are unable to account for the rise in vapour-pressure during the first twenty minutes at 340°, and not at 320°; had it occurred also at 320° we should have ascribed it to the usual rise of pressure accompanying dissociation before equilibrium is established; but, as will afterwards be shown, dissociation is complete at both temperatures; there is no doubt, however, that the temperature of the ammonium chloride must have been greatly lowered at first by volatilization, and it may be due to this cause.

Since at 320° the initial pressure is the same as that obtained by recalculation, the numbers first given for the lower temperatures, and probably for 330° may be considered as correct.

The mean results at 320° and at 340° are :—

Temperature.	Pressure.
	millims.
320	444·7
340	759·6

Some of the experiments described above were made with ordinary commercial ammonium chloride; but the later ones were all made with material prepared from pure hydrochloric acid and "volcanic" ammonia, which, as is known, is free from hydrocarbons.

§ 48. TEMPERATURES of Volatilization of Ammonium Chloride.

A very clear block of commercial ammonium chloride was cut into pieces of suitable size, each of which was drilled with a hole to receive the bulb of the thermometer, and was then cut into a cylindrical shape. Owing to the very high temperature attained by the ammonium chloride, and the sudden heating, the thermometers were frequently broken; each thermometer was carefully calibrated before air was introduced, and their readings served so far to check each other. Although this method appears somewhat crude, yet the concordance of the results to be given shows its reliableness.

SERIES I.—Pressure Raised by Admission of Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
5·9	199·3	65·0	256·6	449·8	315·5
6·2	202·5	74·9	259·0	495·2	319·4
30·2	237·9	81·9	262·6	520·1	320·5
37·9	240·7	89·8	264·1	596·6	325·6
38·1	241·3	100·6	267·7	640·9	327·7
45·6	247·8	109·9	269·9	709·6	331·3
59·9	252·8	122·1	273·3	760·3	333·4

SERIES II.—Pressure Raised by Admission of Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·4	178·5	16·9	220·5	349·8	307·3
1·5	179·3	25·3	229·9	399·5	311·9
2·2	183·3	31·6	235·9	400·4	313·2
3·1	187·5	41·0	244·4	447·7	315·2
3·6	191·1	82·8	263·9	499·8	318·9
4·4	194·7	95·5	266·7	502·5	320·9
4·5	196·8	125·8	275·9	553·7	321·8
4·5	193·3	150·7	280·3	602·3	324·0
8·3	202·1	194·5	289·3	652·6	327·0
9·1	206·0	201·0	289·0	652·9	327·8
12·6	212·2	249·7	296·0	707·7	329·5
16·1	219·6	293·0	302·6	763·3	330·7
16·3	220·5	300·9	302·2		

SERIES III.—Pressure Raised by Admission of Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
3·3	191·7	112·8	273·0	457·7	318·5
6·1	204·6	169·6	284·7	510·3	321·4
9·7	211·4	180·1	287·4	574·5	325·8
20·8	226·9	217·2	292·8	589·9	327·1
37·7	242·5	305·0	303·5	640·4	329·5
65·5	257·1	322·8	306·3	720·2	333·9
77·1	262·4	383·0	311·5		
113·4	272·6	443·0	316·2		

SERIES IV.—Pressure Raised by Admission of Hydrogen Chloride.

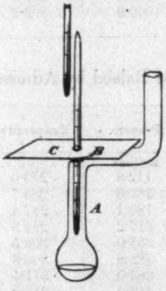
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
3·9	195·5	77·0	261·2	292·4	301·7
12·0	214·7	102·6	267·3	304·6	302·2
19·3	224·2	123·6	273·4	362·9	308·1
31·5	236·9	135·4	277·0	426·3	314·0
34·1	239·3	146·7	278·8	489·3	319·4
42·4	244·5	171·0	283·5	496·7	318·4
57·8	253·2	206·2	290·0	614·4	326·3
70·7	258·9	253·4	296·2	705·7	331·7

During these experiments the tube was jacketed with the vapour of boiling mercury; the readings are given in arithmetical order, but were taken sometimes with rising, sometimes with falling pressure.

§ 49. The results of all these experiments are shown in Plate 1; where it will be seen that the curve representing the temperatures of volatilization under different pressures is sensibly identical with that representing pressures of dissociation and vapour-pressures at different temperatures.

§ 50. It will be noticed that at the highest temperatures the numbers representing temperatures of volatilization fall below the vapour-pressure curve: and since the temperatures of the jacket of mercury-vapour used for heating the block of ammonium chloride was only about 20° higher than the highest temperatures registered by the thermometer imbedded in the block, it was deemed advisable to make an independent determination of the temperature of vaporization under normal pressure. For this purpose a calibrated thermometer into which air had been admitted was heated with mercury-vapour under circumstances as similar as possible to those of the actual experiment. In the woodcut, A represents a wide tube bent twice at right angles, with a bulb blown at one end. At B a hole was blown, to admit the thermometer, which was kept in position by a plug of asbestos. The upper part of the thermometer was protected from hot air-currents by a sheet of asbestos cardboard, C; the mean temperature of the upper part of the stem of the thermometer was ascertained in the ordinary way. The result was as follows:—

Fig. 3.



Reading of thermometer	351·0°
Stem heated by mercury-vapour up to graduation .	110°
Mean temperature of upper portion of stem . . .	33°
Correction for calibration at 351°	− 3·65°
Rise of zero-point owing to heating	1·9°
Corrected temperature	351·0°+12·3°−3·65°−1·9°=357·85°
Barometer	762·1 millims. at 0°
From REGNAULT's table, interpolated.	Temperature=357·6°*

This close approximation between a mercurial thermometer and an air thermometer might excite surprise; but we have frequently noticed that these particular German-glass thermometers give results closely agreeing with air thermometer readings up to 280°. It may be concluded that the temperatures shown by this thermometer, corrected in this way, are in sufficiently close agreement with those of **Regnault's** air thermometer.

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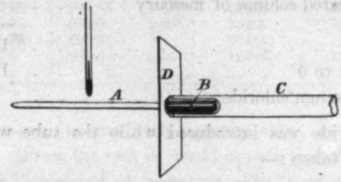
* From our revised table, 358·3°.

§ 51. The temperature of volatilization of ammonium chloride was then determined under ordinary pressure with the apparatus shown in the wood-cut (fig. 4). A block of ammonium chloride, B, was drilled with a hole to receive the bulb of a thermometer, A, and was placed horizontally at one end of an open combustion-tube, C. The stem of the thermometer was protected by a sheet of asbestos, D. The block was heated by applying the flame of a **Bunsen** burner to the combustion-tube, and the temperature registered by the thermometer was read, when constant.

Fig. 4.



Reading of thermometer	329·5°
(Stem was heated up to graduation 30°.)	
Mean temperature of cool portion of stem	30·4°
Correction for calibration at 329·5°	−3·65
Zero-point after experiment	Unaltered
Corrected temperature	329·5+14·4−3·65−1·9=338·35°
Barometer	762·1 millims. at 0°

By the barometer-tube method, the mean-pressure at 340° was, as before mentioned, 759·6 millims. The difference, which is less than 2·0°, may well be due to error of experiment.

§ 52. Some Experiments on the Vapour-density of Ammonium Chloride.

These experiments were carried out by **Hofmann's** method at 280° under pressures varying from 85 millims. to 135·8 millims. The pressure of the vapour in contact with solid, at 280°, is about 145 millims. This temperature is perhaps the only one in which **Hofmann's** method can be applied; for at higher temperatures the vapour-pressure of mercury becomes too great, and atlower temperatures, the vapour-pressure of ammonium chloride is too small.

No serious error can be introduced by the action of the hydrochloric acid on the mercury, because the volume of the gas is so large, the surface of contact with the solid so small, and the action so slow at that temperature.

The HOFMANN'S tube was exhausted, filled with mercury, and jacketed with bromonaphthalene, boiling at 752·3 millims. pressure; the temperature was, therefore, 280°, at which the vapour-pressure of mercury is 157·35* millims.

I. Height of barometer as read on scale	115·0	millims.
„ mercury in HOFMANN'S tube	272·3	„
Difference	157·3	„
Correction for heated column of mercury	13·3	„
Pressure	170·6	„
Pressure reduced to 0°	169·7	„
Weight of ammonium chloride	0·00434	grm.

The ammonium chloride was introduced while the tube was still hot, and the following readings were taken :—

Height of barometer as read on scale	112·8	millims.
„ mercury in HOFMANN'S tube	359·1	„
Difference	246·3	„
Correction for heated column of mercury	9·3	„
Pressure	255·6	„
Pressure reduced to 0°	254·6	„

The tube containing ammonium chloride carried with it a little air, the pressure of which, at the higher temperature and volume, was calculated to be 0·25 millim.

Volume before addition of ammonium chloride	43·94	cub. centims.
„ after „ „ „	63·50	„
Pressure due to air at smaller volume	169·7 − 157·35	millims.
„ „ larger „	$\frac{12·35 \times 43·94}{63·5} = 8·6$	
Total pressure due to air at larger volume	8·6 + 0·25 = 8·85	„
Pressure due to NH_4Cl	= 254·6 − 157·35 − 8·85 = 88·4	„
Vapour density of $NH_4Cl (H = 1)$	13·29	„
Vapour density of $NH_3 + HCl$	13·37	„

The body is thus seen to be totally dissociated.

II. Weight of substance	0·0087	grm.
Barometer, corrected	749·4	millims.
Temperature of bromonaphthalene vapour	279·8°	
Vapour-pressure of mercury	156·6	millims.

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* In revising proofs, we have substituted for the vapour-pressures of mercury determined by REGNAULT, our revised numbers, which we believe to be more accurate.—[May 22, 1886.]

	Pressure (uncorr.).	Correction for column of hot mercury.	Pressure corrected to 0°.	Pressure due to air.	Pressure of ammonium-chloride vapour.	Volume.	P. V.	Vapour-density.
	millims.	millims.	millims.	millims.	millims.	cub. centims.		°
(1)	140·8	14·1	160·3	3·7	..	41·66	..	..
(2)	286·8	7·6	293·3	2·1	134·6	73·52	9,896	15·09
(3)	286·5	7·5	292·9	2·1	134·2	74·11	9,946	15·06
(4)	286·2	7·4	292·5	2·0	133·9	74·57	9,985	14·96
(5)	285·2	7·2	291·3	1·95	132·75	75·41	10,010	14·92
(6)	282·3	6·7	287·9	1·7	129·6	77·75	10,077	14·82
(7)	281·2	6·45	286·55	1·55	128·4	78·78	10,115	14·77
(8)	286·2	7·5	292·6	1·6	134·4	73·91	9,934	15·04
(9)	287·0	7·75	293·65	2·1	134·95	72·73	9,815	15·23
(10)	280·1	6·5	285·5	1·55	127·35	78·56	10,005	14·94

Of these determinations, (1) was with mercury alone, in order to determine the amount of air present. From the rest it would appear that the vapour of ammonium chloride is not wholly dissociated at pressures near those of saturation; the percentage number of molecules decomposed varying from 75·57 to 81·04 within the limits of these experiments. It may also be noticed that, in general, the higher the pressure, the higher the vapour-density.

§ 53. In the case of ammonium chloride it appears that the temperature of volatilization depends on the pressure, and that the curve representing the temperatures of volatilization under different pressures is coincident with that representing the vapour-pressures at different temperatures. But on inspecting the curve (Plate 1) showing the relation between temperature and pressure for ammonium chloride it will be noticed that the temperatures of volatilization, represented by crosses, lie in all cases lower than the circles representing pressures. Two corrections have not been applied, both of which would raise the temperatures of volatilization, because we were unable to estimate the exact amount. The temperatures of volatilization were ascertained by means of a mercurial thermometer, but the others, indirectly by an air thermometer. The thermometers were not compared beforehand, and, having been broken during the experiments, a comparison is now impossible. Thermometers belonging to the same batch, which were made of German soda-glass, have been subsequently compared, and to make their readings coincide with those of an air thermometer require to have their readings raised 1·0° at 220°, 1·2° at 230°, 1·4° at 250°, and 1·5° at 280°. If this correction were applied it is obvious that the results of the two methods would form the same curve. Above 280° this comparison has not been made.

Another correction would appear to be requisite for the highest temperatures, owing to the temperature of the jacket of mercury-vapour being too near that of the block of ammonium chloride. Of this we can form no estimate, but it should be noticed that the single observation at the atmospheric pressure, by a method which is free from both these objections, agrees closely with the point obtained by the barometer-tube method. This is shown by the large cross on the diagram.

§ 54. *Phthalic Acid*, $C_6H_4(COOH)_2$.—This acid melts at 184° (LOSSEN), decomposing into water and phthalic anhydride, $C_6H_4(CO)_2O$. ADOR ('Annalen,' 163, p. 230) states that large crystals melt at 213°, while, when powdered, the melting-point is 203°.

PRESSURES of Dissociation of Phthalic Acid in Barometer-tube.

Temperature.	Pressure.	Duration of experiment.
°	millims.	′
30·8	4·7	19
59·8	20·8	46
78·0	28·8	62
100·0	41·2	84
116·0	51·9	140
131·95	61·7	151
131·6	60·1	125
143·6	111·9	423
149·9	164·6	384
149·8	163·1	18
154·9	215·5	363
159·5	327·3	257
164·6	443·2	142

The tube was here refilled, as the original quantity of substance was deemed insufficient; the remaining numbers of this series will be referred to under succinic acid.

Temperature.	Pressure.	Duration of experiment.
°	millims.	
165·3	514·3	67′
168·7	629·6	Constant
Recombination 165·0	518·7	122′
168·1	618·7	118′

The results of these experiments are graphically represented in Plate 2. The form of the curve appears to differ somewhat from that of an ordinary vapour-pressure curve, for the curvature is more abrupt on approaching the horizontal portion. This peculiarity will be referred to later.

§ 55. TEMPERATURES of Volatilization of Phthalic Acid.

As phthalic acid dissociates on liquefying, the bulb of a thermometer was first covered with cotton-wool, and dipped repeatedly into a boiling aqueous solution of the acid. The thermometer was then hung in a bell-jar over sulphuric acid for several days until dry. The requisite temperature was obtained by jacketing with vapour of bromonaphthalene, boiling at about 280°. The condenser was cooled by a freezing mixture.

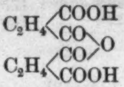
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·05	191·9	9·8	201·7	87·3	196·9
3·5	198·4	142·0	210·1	32·2	168·6
6·4	199·4	46·9	177·1		
30·4	202·9	22·8	159·5		

When the pressure was raised to 142 millims. the anhydride was left behind, and condensed as liquid on the sides of the tube, crystallizing on the colder parts. After the experiment, on removing the freezing mixture, the solid which had passed into the condenser liquefied partially, the liquid containing crystals. There had therefore been a separation of water. The solid in the condenser was evidently acid, and not anhydride, so that at very low pressures the acid had passed over undecomposed: it was then only after the pressure had been raised that decomposition took place, and it is probable that the substance had then melted, though it was difficult to observe this on the cotton-wool. The phthalic acid condensed in very small crystals, forming an opaque mass: the anhydride, in long transparent crystals. There was a distinct line of demarcation between the two. The last five numbers, which differ entirely from the others, are evidently the temperatures of volatilization of the anhydride, and the former ones of the acid. These numbers are reproduced in a separate curve. The temperatures of volatilization of the acid are plotted in Plate 2, and it is to be observed that, although there is an indication of a curve of the usual form, it completely differs from that obtained by the other method.

§ 56. *Succinic Acid*, $C_2H_4(COOH)_2$.—This acid melts at 180°, and is said to boil at 235° with formation of the anhydride, $C_2H_4(CO)_2O$. The acid used in these experiments was recrystallized, and kept over phosphoric anhydride.

PRESSURES of Dissociation of Succinic Acid in Barometer-tube.

A very large number of experiments were made with this substance. In the first three series the numbers obtained gave, when graphically represented, curves with double flexure; and so long as the same amount of substance was employed recombination at any given temperature reached the same point as regards pressure as did decomposition. The curves obtained from these series were fairly concordant. But, on increasing the amount of substance, the pressures for given temperatures were much higher, and the double flexure tended to disappear. With phthalic acid it is possible that the vertical trend of the curve might have been due to an insufficient amount of substance; but this cannot have been the case with succinic acid. As the pressure of dissociation of succinic acid appears to depend on the amount of substance present, and is capable of being altered at will, and as the number of experiments made on this subject comprise several thousand readings, and lasted over six weeks, we content ourselves with reproducing the results in the form of curves. (See Plate 2.) It may be generally stated that the larger the amount of substance the higher the pressure at which the double flexure appears. It may possibly be that succinic acid has the power of forming intermediate anhydrides of some such type as



and that its abnormal behaviour is to be accounted for on the supposition of their existence, but this is merely a conjecture.

§ 57. TEMPERATURES of Volatilization of Succinic Acid.

The bulb of the thermometer was dipped repeatedly into the melted acid until a sufficiently thick layer had accumulated. For low pressures the condenser was cooled by a freezing mixture, and the tube was jacketed with vapour of methyl salicylate.

SERIES I.

Pressure.	Temperature.
millims.	°
0·9	153·7
2·3	166·8
2·5	169·3

SERIES II.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·55	160·7	6·4	174·7	75·4	175·1
1·65	161·5	7·4	176·0	107·8	174·3
1·70	161·0	12·5	176·8	139·3	174·1
1·90	162·4	15·6	176·1	168·7	174·2
2·1	162·4	17·1	176·5	220·4	174·5
3·0	167·3	30·9	175·6	275·1	174·5
4·3	170·2	51·1	175·8		

The substance melted after the pressure had been raised to 275·1 millims.; the melting-pressure must therefore occur between the pressures 220·4 and 275·1 millims. After the experiments were finished the melting-point of the acid still adhering to the thermometer bulb was compared with that of the original substance, and they were found to be identical at 181·0°. Here, again, it is noticeable that the results of the two methods are widely divergent. (Plate 2.)

§ 58. *Aldehyde-Ammonia*, $CH_3.CH\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$.—This substance was suspected to decompose on heating, in spite of SCHRÖDER's having found its vapour-density normal at 160° ('Berichte,' 4, p. 470); and it will be seen later that our experiments prove the justice of this conclusion. The substance smells at once of aldehyde and ammonia. It is said to melt between 70° and 80°, and to distil undecomposed at 100°.

§ 59. PRESSURES of Dissociation in Barometer-tube.

Temperature.	Pressure.	Duration of experiment.
°	millims.	
21·3	7·0	12 hours.
28·9	13·5	83 minutes.
39·7	32·9	88 ,,
45·2	49·8	27 ,,
50·0	83·6	Not constant after 249 minutes.
54·6	144·2	,, ,, 718 ,,
55·7	176·2	Constant after 75 minutes.
60–60·8	307 4	Not quite constant after 25 hours.

It was evident from the discoloration of the substance at the higher temperatures that it had partly decomposed; the results, however, point to gradual dissociation, accompanied at the higher temperatures with some decomposition. The curve is given in Plate 2.

§ 60. TEMPERATURES of Volatilization of Aldehyde-ammonia.

The condenser was cooled by a freezing mixture. The thermometer-bulb was covered with cotton-wool, and dipped repeatedly into the melted substance. The tube was jacketed with the vapour of chlorobenzene.

SERIES I.—Pressure raised by admitting Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
2·8	26·1	33·0	56·2	403·3	78·2
3·25	29·2	63·4	61·5	53·3	60·3
3·85	33·2	124·1	67·2	511·1	81·2
8·5	42·7	265·0	74·2		

SERIES II.—Pressure raised by admitting Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·95	24·3	95·5	65·1	349·3	76·7
2·4	27·1	161·3	69·2	153·2	68·8
2·8	28·9	198·1	70·9	445·7	79·2
12·9	47·1	250·9	73·1		
21·6	52·6	300·4	74·9		

SERIES III.—Pressure raised by admitting Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
6·3	38·2	38·0	59·0	185·0	72·2
6·45	39·55	53·7	61·2	216·3	73·2
9·5	44·3	67·8	63·2	249·5	74·8
10·8	46·3	79·5	64·5	278·3	75·9
12·55	48·2	95·6	65·4	205·2	73·4
15·6	50·5	114·0	67·2	140·1	70·3
21·5	53·7	136·0	68·7		
28 6	56·6	156·5	70·2		

SERIES IV.—Pressure raised by admitting Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	
4·0	35·6	44·0	60·2	229·8	73·9
21·4	52·2	53·3	62·1	303·6	76·2
48·8	60·2	81·7	66·0	300·1	76·0

SERIES V.—Pressure raised by admitting Ammonia-gas.

Pressure,	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
9·7	42·3	150·3	69·2	551·4	81·4
11·1	45·1	239·4	73·1	606·3	82·8
23·5	52·6	314·9	75·3	641·8	83·2
66·8	62·3	382·0	77·2	711·7	85·2
68·8	63·0	435·5	78·6	736·1	85·8
108·2	66·6	506·4	80·3		

SERIES VI.—Pressure raised by admitting Aldehyde-vapour, prepared at the time from Aldehyde-ammonia and Sulphuric Acid, and dried over P_2O_5.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.		millims.		millims.	
8·45	42°·1	67·5	63°·9	309·9	75°·1
10·15	44·3	99·7	65·8	348·1	76·3
23·6	54·2	139·8	68·8	403·1	77·7
37·7	59·1	175·1	70·8	462·4	78·9
44·4	61·0	215·8	72·1	553·1	80·3
49·8	62·0	266·0	73·9	616·9	81·4

When air or aldehyde was admitted to raise the pressure the cotton-wool became discoloured by a brown resinous substance; this was not the case when the pressure was raised by admitting ammonia-gas (LIUBAWIN, 'Berichte,' 8, p. 1684). Although the results obtained on raising pressure with air, ammonia, and aldehyde are somewhat divergent, yet a very large difference of pressure is caused by a slight alteration in temperature, and the results of observations with any one of these substances show equal discordance among each other. This is not surprising considering the nature of the compound. (Plate 2.)

§ 61. VAPOUR-DENSITIES of Aldehyde-ammonia.

The vapour-densities were determined by HOFMANN'S method at 78·25° and at 131·8°.

Weight.	Temperature.	Pressure.	Volume.	P.V.	Vapour-density.	Percentage number of molecules decomposed.
		millims.	cub. centims.			
0·0353	78°·25	294·1	73·06	21,487	17·93	70·11
„	„	280·0	76·86	21,521	17·90	„

A long time had to elapse before pressure became constant and the vapour acquired its maximum volume.

Weight.	Temperature.	Pressure.	Volume.	P.V.	Vapour-density.	Percentage number of molecules decomposed.
		millims.	cub. centims.			
0·0353	131°·8	324·1	79·78	25,857	17·17	77·64 (?)

A certain amount of yellow resin had deposited on the surface of the mercury at the higher temperature, which accounts for the dissociation being apparently incomplete. At the lower temperature no decomposition was observed.

The dissociation of this substance was evidently far from complete, and it will be seen that the curve representing temperatures of volatilization approaches more nearly to the usual form of a vapour-pressure curve. The pressure, 280–290 millims., lies considerably below that obtained by the still method at 78·25°, which is about 420 millims., and it is very far below saturation, as indicated by experiments with the barometer-tube.

§ 62. *Paraldehyde and Metaldehyde.*—It was thought that some results might have been obtained from these substances. Paraldehyde is a liquid of the formula $C_6H_{12}O_3=3C_2H_4O$, obtained by treating aldehyde with a minute quantity of sulphurous anhydride, cyanogen, or certain other substances. Its vapour-density is said to be normal for the formula $C_6H_{12}O_3$ (BEILSTEIN, 'Handbuch der Organischen Chemie,' p. 28). It boils at 124° (KEKULÉ and ZINCKE), at 123·2° to 123·5° (BRÜHL). When distilled with a little sulphuric acid it changes totally to aldehyde (WEIDENBUSCH).

A portion boiling at 122·6° was employed for the following experiments. When heated in a barometer-tube it was found to attack the mercury; it was therefore well shaken with mercury and redistilled. The pure substance does not appear to decompose, and the results obtained by the two methods were practically identical.

Metaldehyde is a solid crystalline body, produced by the action of gaseous hydrogen chloride, or sulphurous anhydride on aldehyde in a freezing mixture. It is insoluble in the ordinary solvents, and sublimes without melting at 112–115°, and when heated under pressure to 120° it changes completely into aldehyde. Its dissociation-pressure was determined in a barometer-tube.

Temperature.	Pressure.	Time.
°	millims.	
17·0	11·8	24 hours
50·4	282·0	216′
"	332·0	216′+380′=596′
"	339·4	596′+75′=671′

The rise of pressure was 2·4 millims. in the last 35′.

Temperature.	Pressure.	Time.
°	millims.	
60	459·0	335′

The pressure rose 14·3 millims. in the last 60′.

We have evidently here to deal with a substance the equilibrium of which is established only after a very long time. It was allowed to cool, and stood for ten days; combination was gradually taking place, as shown by the gradual rise of the mercury.

§ 63. *Nitrogen Peroxide.*—This substance was prepared in the following manner. A mixture of arsenious oxide, sulphuric acid, and nitric acid was heated; the vapour evolved was led through a U-tube containing arsenious oxide, and then through a drying-tube filled with phosphoric anhydride. It then entered a U-tube, provided with a bulb, which was placed in a freezing mixture. To avoid decomposition, the apparatus was constructed, as far as possible, in one piece. After redistillation the substance, which had a deep-red colour, was used for the following experiments.

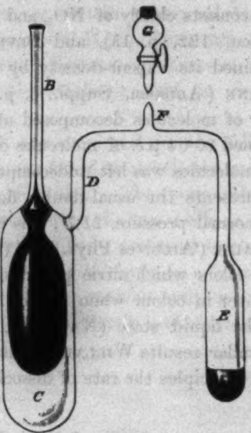
The vapour-density of nitric peroxide in presence of nitrogen was first determined by PLAYFAIR and WANKLYN ('Annalen,' 122, p. 249). From their results they concluded that at 100° the gas consists chiefly of NO_2, and at the ordinary temperature of N_2O_4. MÜLLER ('Annalen,' 122, p. 15), and DEVILLE and TROOST ('Comptes Rendus,' 64, p. 237) determined its vapour-density by DUMAS' method, with very concordant results. NAUMANN ('Annalen,' Suppl., 6, p. 203) calculated from their data the percentage number of molecules decomposed at different temperatures, and found that at 26·7° it contained 80·04 p.c. of molecules of N_2O_4; while at 135°, 1·31 p.c. of the total number of molecules was left undecomposed. The curve constructed from NAUMANN'S numbers presents the usual double flexure of a dissociation-curve. At the boiling-point, under normal pressure, 21·7°, it is evident that less than 20 p.c. is dissociated. DE LA FONTAINE ('Archives Phys. Nat.' (2), 28, p. 271) drew attention to the remarkable change of colour which nitric peroxide gas shows on heating; and as the liquid also grows lighter in colour when cooled, it appears probable that dissociation still proceeds in the liquid state (NAUMANN, 'Thermochemie,' ed. 1882, p. 138). From these and similar results WILLARD GIBBS has constructed a formula, showing on thermodynamical principles the rate of dissociation of nitric peroxide.

§ 64. VAPOUR-PRESSURES of Nitric Peroxide.

As liquid nitric peroxide quickly attacks mercury, it was impossible to determine its vapour-pressure by the usual method. Tolerably accurate results were obtained by the following device. An apparatus of the form given in the annexed drawing was employed.

A large bulb A of about 50 ccs. capacity, very thin walled, yet strong enough to resist the pressure of the atmosphere, was sealed to a graduated glass tube of thermometer-bore, B, and was fused into an encasing bulb, C, the walls of which were much thicker. From the upper part of C a tube, D, projected vertically for some distance, and was then bent twice at right angles. The other extremity of this tube was enlarged at E; a T-piece, F, was sealed to the horizontal portion of the tube; the bulb A was filled with mercury, by exhausting it, and allowing mercury to enter. The bulb C was placed in a vessel with a perforated bottom, containing finely-pounded ice, which was heaped round the lower portion of the graduated stem, and continually renewed. As the bulb A forms an extremely delicate thermometer, in which 60° of the arbitrary scale corresponded to 1° of temperature, it was only after several hours that the temperature became constant. When absolute constancy of temperature had been attained, the T-tube F was connected with the pump and with a gauge, and air was removed from the apparatus; the diminution of pressure caused the bulb A to expand, and the mercury in the graduated stem to fall. This fall was found to be sensibly equal for equal decrease of pressure; and from the mean of a great number of readings a change of 9·04 millims. pressure was found to be equivalent to 1° of the scale; hence $\frac{1}{10}$° corresponded to about 1 millim.

Fig. 5.



A perfectly air-tight stopcock was then fused on to the T-tube F, and the apparatus was dried by exhausting the air with a Carre's pump. The apparatus was then pumped empty of air with the mercury-pump, and the stopcock was closed. A reservoir, G, which had been sealed to the stopcock, was then filled with liquid nitric peroxide, and the stopcock was opened so as to admit two or three cubic centimetres of the liquid. The stopcock was then closed, and removed by sealing.

As the height of the mercury in the graduated stem had been read before introducing the nitric peroxide, and as the introduction of the liquid caused a rise of the mercury corresponding to the pressure of its vapour, the apparatus acted as a barometer for temperatures below 0°. The vapour-pressure was regulated by the coldest part of the apparatus. The bulb E was placed in a well-stirred mixture of ice and hydrochloric acid, in contact with a thermometer, and the temperature and the position of the mercury in the graduated scale were read, with the following results:—

§ 65.

Scale readings.*	Pressure.	Temperature.
	millims.	°
115·0	68·6	−26
114·9	69·6	−25·2
113·3	84·6	−21·0
112·0	96·0	−19·1
112·0	96·0	−18·0
111·4	101·6	−17·0
108·0	132·2	−13·0
106·1	149·4	−11·5
106·0	150·2	−11·0
105·4	155·7	−10·0
105·8	152·0	− 9·6
104·7	161·7	− 8·7
104·1	167·5	− 8·0
100·5	200·0	− 5·3
97·7	225·3	− 3·1

§ 66. To obtain readings at a higher temperature, the bulb C was placed in running water, the temperature of which was almost constant, and mercury was removed from the graduated stem for convenience in reading. The readings obtained by this method correspond with those obtained by the still-method, to be hereafter described. It was accordingly assumed that they would correspond at 0°. The bulb E was placed in melting ice, and the position of the mercury in the graduated stem was noted. The ice round E was now replaced by running water at a temperature of 13·9°, and the alteration in position of the mercury in the scale read. Since the temperature of the running water was not absolutely constant, this was repeated several times, and the mean result taken as correct. It was found as the mean of six experiments that an alteration of temperature from 0° to 13·9° produced a rise of mercury of 30·9 scale divisions, corresponding to an increase of pressure of 279·3 millims. As the pressure at 0° found by the other method is 257·5 millims., the pressure at 13·9° is therefore 279·3+257·5=536·8 millims.

§ 67. A direct reading at 19·6 was taken by placing the apparatus in a large tank of water of that temperature, the temperature of the room being some degrees higher. The mercury in the scale read 81·0°. The point of the T-tube was broken, so as to communicate with the atmosphere, and the height of the mercury was again read. It was 73·2°. This difference was 7·8°, or allowing for the cooling of the water during one minute, 7·7°. Multiplied by 9·04, this difference is equivalent to 69·5 millims. Subtracting from the pressure of the atmosphere at the time, 756·6, the true pressure in the apparatus was found to be 687·1 millims.

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* It should be mentioned that the scale was inverted, so that a lower reading corresponds to a higher pressure.

§ 68. MAXIMUM Temperatures at Different Pressures.

In these experiments the only differences from the ordinary arrangement were—a stopcock was used instead of an indiarubber tube and clip to admit the liquid; as nitric peroxide attacks cotton-wool, the bulb of the thermometer was covered with asbestos; warm water was used as a jacket, and the condenser was placed in a good freezing mixture.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
86·5	−19·35	257·5	0·0	483·0	12·1
91·8	−18·15	291·0	+2·2	536·0	14·2
113·5	−14·60	316·5	4·0	578·5	15·8
127·0	−12·7	344·0	5·7	613·5	17·0
147·5	−10·0	390·5	7·9	660·5	18·5
177·0	− 6·7	426·0	9·7	738·5	20·9
204·5	− 4·3	467·5	11·4	752·0	21·5

§ 69. On reference to the curves (Plate 1) it will be seen that the results by both methods agree as closely as could be expected from the nature of the first. In this respect the behaviour of nitrogen peroxide is similar to that of ammonium chloride; but while the latter is completely dissociated at its volatilizing point under normal pressure, the former has suffered only very partial dissociation.

NOTE.—Quite recently E. and L. NATANSON ('WIEDEMANN'S Annalen,' 24, p. 454) have determined the relations between the specific heat and vapour-density of nitrogen peroxide under varying pressures, and at a constant temperature. They find that while the vapour-density increases, the specific heat decreases with rise of pressure, and conclude from this that the alteration of density of nitrogen peroxide is due to the dissociation of N_2O_4 into $2NO_2$.

§ 70. *Acetic Acid.*—The sample of acetic acid used was the same as that employed by us in determining the different vapour-pressures of the solid and liquid acid (see 'Transactions,' 1884, Part II.). It was perfectly pure, boiling with absolute constancy at 118·7°, at a pressure of 765·2 millims., and melting at 16·4°. The large stock of acid contained a little water; but on fractionation, after one-third had distilled over, the remainder always boiled constantly to the last drop. The various determinations were made with portions fractionated at different times.

PLAYFAIR and WANKLYN (Trans. Roy. Soc., Edin., 22, Part III., p. 441) were the first to suggest that, as the vapour-density of acetic acid at low temperatures is nearly double that which it possesses at high temperatures, its formula at low temperatures is $C_4H_8O_4$; and that on heating, this molecule splits into two of the formula $C_2H_4O_2$. An increase of density in the neighbourhood of the condensing-point is a common property of all gases; and NAUMANN concludes ('Annalen,' 155, p. 325) that, although acetic acid may exhibit this behaviour, yet that its abnormal density is to be explained chiefly on **Playfair** and **Wanklyn's** supposition. **Horstmann** and others take the opposite view. So far, then, it is an open question whether acetic acid dissociates or not.

§ 71. Numerous determinations of the vapour-pressures of acetic acid have been made by **Regnault** ('Mémoires de l'Académie', xxvi., p. 51–60), **Bineau** ('Annales' [3], 18, p. 226), **Landolt** ('Annalen,' Suppl., 6, p. 157), and **Wüllner** (Pogg. Ann., 103, p. 529). Their results show absolutely no concordance. Thus at 15°, **Bineau** finds a vapour-pressure of 7 millims.; while **Landolt** finds 15 millims.; and **Regnault's** determinations vary from 8·5 millims. to 10·4 millims. At higher temperatures the various determinations are even less concordant. At 80°, for example, the difference between determinations by **Landolt** and by **Wüllner** amounts to 85 millims. **Regnault** attributed his discordant results to the presence of water in those samples which gave a lower pressure, and of acetone in those giving a higher pressure. It will be seen that our very numerous determinations exhibit perfect accordance with each other. The vapour-pressures and the temperatures of volatilization at low temperatures have already been given by us in the paper referred to; above 20° the results are as follows:—

§ 72. Vapour-pressures of Acetic Acid in Barometer-tube.

Series I.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
21·2	12·7	39·2	32·2	63·2	100·7
24·5	14·6	43·8	39·7	66·0	113·4
29·15	18·55	48·1	49·9	68·7	127·7
31·0	20·45	51·5	58·7	71·1	142·5
33·2	23·2	54·9	68·3	73·4	157·0
34·4	24·25	57·6	77·4	75·5	170·1
35·6	26·45	60·2	88·5	78·1	190·7

Series II.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
25·9	15·05	45·1	42·65	66·15	114·6
28·3	17·7	49·6	52·9	68·15	126·0
30·95	20·25	53·2	63·6	70·05	136·1
34·3	25·25	57·0	75·5	72·95	153·6
37·4	29·2	59·9	86·5	74·6	164·5
40·8	34·5	63·2	101·2	77·95	188·1

After the completion of these experiments it was found, on inclining the tube, that absolutely no air was present.

SERIES III.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
62·5	97·2	93·7	340·0	108·3	551·6
74·3	163·4	105·2	499·9	109·3	574·4
83·0	229·9	94·1	345·6	..	..

§ 73. MAXIMUM Temperatures at Different Pressures.*

SERIES I.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
236·3	83·9	78·7	57·4	28·3	36·1
194·4	78·8	66·7	53·5	22·9	32·7
156·2	73·2	53·7	49·2	16·8	27·2
131·9	69·1	51·7	48·5	12·9	22·4
96·3	61·8	41·7	43·8		

SERIES II.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
146·3	71·6	34·3	40·1	17·45	27·3
58·1	50·5	28·9	36·9	12·65	21·4
51·3	48·2	21·8	31·3		

SERIES III.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
14·5	23·4	14·35	23·0	12·45	20·9

SERIES IV.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
15·95	25·6	13·05	22·05	12·85	21·68

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* In this case, as well as in that of nitric peroxide, it is inadmissible to use the expression "temperature of volatilization," which by definition applies only to solids. (Phil. Trans., 1884, I.) Nor is "boiling-point" a correct term, for ebullition does not take place. With liquids which are known not to dissociate, the expression "vapour-pressure" may of course be used.

SERIES V.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
717·9	117·15	460·3	103·3	242·1	84·6
657·5	114·1	425·2	100·6	228·0	83·4
642·6	113·4	396·3	98·6	215·2	81·65
623·8	112·4	376·4	97·4	199·5	79·8
587·1	110·4	344·3	94·5	177·3	76·4
540·0	107·45	307·9	91·4	127·5	68·5
501·8	105·45	267·8	87·5	87·6	59·6
				55·6	49·65

The shortness of series III. and IV. is accounted for by the fact that they consist of the higher numbers of series which have been elsewhere given. The results by both methods are shown in Plate 2.

§ 74. It was thought possible that the hydrochloride of ethylamine, and that chlorine hydrate might yield serviceable results. The former gave off a permanent gas, and grew pasty when heated; the temperature rose steadily to above 300° with no sign of a check.

The chlorine hydrate, prepared by bringing a thermometer-bulb covered with cotton-wool, and soaked with water, in contact with chlorine at a low temperature, melted suddenly when the pressure was lowered, with rapid evolution of chlorine, while the temperature rose to 0°. This unusual behaviour perhaps deserves further investigation,* but as it did not come under our programme, it was not further followed.

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* (Since writing the above, the matter has been made the subject of experiment by H. LE CHATELIER, "Comptes Rendus," 99, p. 1074; he finds that solid chlorine hydrate has a higher vapour-pressure than the liquid hydrate, if the latter exists, and is not a mere solution of chlorine in water. It may be remembered that similar results with chloral ethyl- and methyl-alcoholates are described by us in § 25).

§ 75. Discussion of Results.

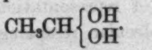
For the sake of clearness we tabulate the results already described :—

Name of substance.	Vapour-density shows—	Temperature of volatilization.	Vapour-pressure, or pressure of dissociation.
Chloral hydrate	Dissociation almost complete at 78°	Independent of pressure	Curve of ordinary form.
Butyl chloral-hydrate . .	Complete dissociation at 160°	Independent of pressure	Curve of ordinary form.
Chloral methyl-alcoholate	At 78·5°, about 78 per cent. dissociated	Independent of pressure	Curve of ordinary form.
Chloral ethyl-alcoholate .	At 78°, 82·5 to 83 per cent. dissociated	Independent of pressure	Curve of ordinary form.
Ammonium carbamate .	Total dissociation . . .	Constant at about 65° under all pressures	Curve of ordinary form.
Ammonium chloride . .	Dissociation very nearly complete at 280°	(Curves	identical.)
Phthalic acid	Vapour-density not determined; dissociation probably very large, no constant melting-point	Rudimentary curve at low pressures	Abrupt change of direction of curve.
Succinic acid	Vapour-density not determined; dissociation probably less complete than with phthalic acid, constant melting-point	Curve more obvious than with phthalic acid	Appears to depend on amount of substance present; curve shows double flexure.
Aldehyde-ammonia. . .	70 per cent. dissociated at 78·25°, under reduced pressure	Curve of usual form .	Curve of usual form, but pressure higher than by other method.
Paraldehyde	No dissociation	(Curves	identical.)
Metaldehyde	. . . .	. . . .	Equilibrium established only after very prolonged heating.
Nitrogen peroxide . . .	Dissociation small below 20°	(Curves	identical.)
Acetic acid	Vapour - density abnormally high, especially at low temperature	(Curves	identical.)
Ethylamine hydrochloride	No results		
Chlorine hydrate . . .	No results		

§ 76. It is evident that these substances may be divided into two groups: that in which the curves representing temperatures of volatilization and vapour-pressures are identical; and that in which these curves are distinct. The members of the first class behave like ordinary solids and liquids; and the class includes the three substances, ammonium chloride, nitrogen peroxide, and acetic acid; with the first of these dissociation is nearly complete sixty degrees below the temperature of volatilization under normal pressure; with the second dissociation amounts to less than 20 per cent. at its boiling-point; while with acetic acid it is uncertain whether true dissociation takes place. The second group, which contains the rest of these substances, with the exception of paraldehyde, which is stable, may be divided into two sections: that in which pressure has no apparent influence on the temperature of volatilization, and that in which its influence is partial.

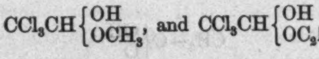
§ 77. Judging from the determinations of vapour-density which have been made, it may fairly be stated that those substances which show the greatest amount of dissociation also show the greatest divergence between the curves, and the least connexion between pressure and temperature of volatilization. Thus with chloral hydrate, the dissociation of which is almost complete, the temperature of volatilization is independent of pressure, and with ammonium carbamate, which is completely dissociated, this is also noticeable. Again, with succinic and phthalic acids, the former of which, judging from its melting-point, is probably more stable than the latter, the curve representing temperatures of volatilization of the former is more obvious than that of the latter; and with aldehyde ammonia, the two curves of which have the same general form and which are not widely divergent, the determination of vapour-density shows that the dissociation is only 70 per cent. at 78·25°, under greatly reduced pressure. Again, with the alcoholates of chloral, which appear to show the same behaviour as chloral hydrate in the still, the melting-pressure is so low, and the rate at which they volatilize so rapid, that any small indication of temperature being influenced by pressure might well have escaped observation. Moreover, we are not able at present to compare the relative stability of these bodies with that of phthalic and succinic acids. Had we to deal with this class alone it would have appeared that the statement at the beginning of this paragraph might be general; but ammonium chloride forms so marked an exception that this view can hardly be sustained without qualification.

§ 78. It is also to be noticed that the chloral compounds with water and with the alcohols belong to the class of dihydric alcohols, or their methyl or ethyl derivatives. Thus aldehyde itself, when mixed with water, evolves heat, and undergoes contraction; and this behaviour would point to the formation of the dihydric alcohol



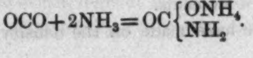
$$CH_3CH\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

Now such a union, if this constitution be accepted as correct, involves the breaking down of a molecule of water, and the partial molecular rearrangement of aldehyde, so that from CH_3CHO there is formed $CH_3CH(OH)_2$. With the methyl and ethyl compounds the substance produced is at once a monohydric alcohol, and a methyl or ethyl ether, thus:—



$$CCl_3CH\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right., \text{ and } CCl_3CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right..$$

In the case of ammonium carbamate its formation involves the breaking down of one molecule of ammonia, and the formation of an ammonium group, NH_4, and of an amido group, NH_2: and this necessitates the actual transfer of an atom of hydrogen from one nitrogen-atom to the other, thus:—



$$OCO+2NH_3=OC\left\{\begin{matrix}ONH_4\\NH_2\end{matrix}\right..$$

Again, aldehyde-ammonia is usually viewed as a dihydric alcohol, in which one hydroxyl group is replaced by an amido group, and this again involves the breaking down of a molecule of ammonia, its formula being $CH_3CH\begin{cases}OH\\NH_2\end{cases}$. Lastly, the combination of phthalic or succinic anhydride with water involves the breaking down of a molecule of water, thus:—

$$C_2H_4(CO)_2O+H.OH=C_2H_4(COOH)_2\ ;$$
$$C_6H_4(CO)_2O+H.OH=C_6H_4(COOH)_2.$$

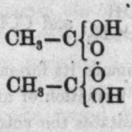
In all these cases the behaviour in the still differs from that in the barometer-tube.

§ 79. The three remaining substances, nitrogen peroxide, acetic acid, and ammonium chloride, give identical vapour-pressures by both methods; and in this their behaviour does not differ from that of stable solids or liquids. It is, therefore, to be surmised that these substances must show some essential difference in constitution from the others, and we shall consider them in detail.

Nitrogen peroxide, when dissociated, may have one of two formulæ, either $N\begin{smallmatrix}=O\\=O\end{smallmatrix}$ or $N\begin{smallmatrix}-O\\ |\\-O\end{smallmatrix}$. It is indifferent for our purpose which is accepted; but, taking the first as correct, there are three ways of representing the union of two molecules of NO_2 to form N_2O_4. First: Simple union of the nitrogen atoms thus:— $\begin{smallmatrix}O=\\O=\end{smallmatrix}N-N\begin{smallmatrix}=O\\=O\end{smallmatrix}$. Second: Union through the oxygen atoms:—$O=N-O-O-N=O$. Third (and the hypothesis has been recently advanced yb **Divers**): Union of a nitrogen atom of the one molecule with an oxygen atom of the other, the result being a nitrate of nitrosyl, $\begin{smallmatrix}O=\\O=\end{smallmatrix}N-O-N=O$.

Now, none of these methods of representation involves the breaking down of a molecule, but only a partial molecular re-arrangement, such as takes place in the aldehyde group, CHO, which does not involve an alteration in position of the atoms.

§ 80. Passing to acetic acid, it has been suggested by **Playfair** and **Wanklyn** that the abnormal vapour-densities point to a molecule of the formula $C_4H_8O_4$, and the formula deduced by **Willard Gibbs** from the observations of these experimenters and others is based on this assumption. If this view is correct, the only structural formula applicable is

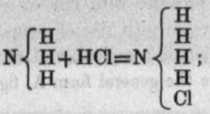


$$\begin{array}{l}CH_3-C\begin{cases}OH\\O\end{cases}\\ \qquad\quad\;\;|\\ CH_3-C\begin{cases}O\\OH\end{cases}\end{array}$$

where the oxygen of the two carboxyl groups forms the connecting link. Here again there is no breaking down of a molecule.

But experiments which we have made on the density of the saturated vapour of this substance show clearly that the density increases more and more rapidly with fall of temperature, until at 50° the density is more than 55, that of the molecule $C_4H_8O_4$ being 60; and some isolated determinations by a method, of the reliability of which we are in some doubt at present, appear to indicate that at 20° the vapour-density may be as high as 70, and there is no doubt that the trend of the curve representing the relation of saturated vapour-density to pressure or temperature would, if prolonged and if no sudden change of direction occurs, give vapour-densities at low pressures and temperatures considerably higher than 60. We have shown in a paper, recently presented to the Society, that alcohol, and also ether, which may be regarded as typical of liquids in general, do not show this increase in the density of their saturated vapours with fall of temperature and pressure. We are at present engaged in a study of the thermal properties of acetic acid, which we hope will definitely decide this point. If the vapour-density of acetic acid is really higher than 60, at low temperatures no structural formula can represent the method of combination of the molecules.

§ 81. The formation of ammonium chloride is usually believed to be attended by the change of valency in nitrogen from triad to pentad, and to be accompanied by the breaking down of the molecule of hydrogen chloride, thus:—



$$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + HCl = N\left\{\begin{matrix}H\\H\\H\\H\\Cl\end{matrix}\right. ;$$

and the existence of the extremely stable phosphorous pentafluoride is a strong argument in support of this view.

But if it be held, there appears no reason why we should not place in the same class potassium hydrogen fluoride, KHF_2, and hydroplatinichloric acid, H_2PtCl_6, and other similar compounds.

On the other hand, such compounds may be placed in the class of "molecular combinations;" but if this be done it must be conceded that such compounds are not always to be distinguished from "atomic combinations" by any ordinary tests of stability.

Now ammonium chloride, although it agrees with acetic acid and with nitrogen peroxide in its behaviour as regards vapour-pressures, differs from them in respect of its dissociating into dissimilar molecules. It is thus evident that the agreement in behaviour of these three substances with that of ordinary solids and liquids cannot be ascribed to the similarity of the molecules produced by dissociation.

§ 82. As nitrogen peroxide and acetic acid in their dissociation do not require a breaking down of a molecule such as water or ammonia, and as ammonium chloride agrees with them in its behaviour as regards vapour-pressure; and as this agreement, as has already been shown, does not depend on the amount of dissociation, for there are some bodies in the other class totally dissociated, and some partially dissociated;

it may be surmised that in the act of combination of ammonia with hydrogen chloride, the molecule of hydrogen chloride is not split but combines as a whole. Should this conjecture not be accepted as correct it will be necessary to seek for an explanation of the phenomena observed, by some relations yet to be discovered. Should it be accepted, the classification of those substances in which an evident molecular rupture takes place, suggested in § 77, may still be adopted; and it is probable that an idea of the amount of dissociation may be gathered from the relation of the two curves.

§ 83. Some points still remain to be discussed.

Vapour-pressures of substances undergoing partial dissociation.—A substance capable of exerting vapour-pressure, and at the same time capable of dissociating, exerts a pressure which is the sum of the vapour-pressures of the undecomposed substance, and of the bodies resulting from its dissociation. If these two pressures could be determined separately by experiment we should have two separate curves, the resultant of which would be that representing the pressure determined by the barometer-tube method.

The curve representing the true vapour-pressure of the dissociating body would, to begin with, show increase of pressure with rise of temperature. But at a certain temperature pressure must decrease with rise of temperature, for if the temperature be sufficiently raised dissociation is complete, and there is no true vapour-pressure. The curve must, therefore, have the general form A, fig. 6 or fig. 7.

At the same time the products of dissociation exert a pressure which increases more and more rapidly with rise of temperature (as in *B*, figs. 6, 7, 8). Now the combination of two such curves might yield a curve of double flexure, as shown in *C*, fig. 6;

and an indication of this may possibly be seen with succinic acid. Or it may give a curve with an abrupt change of direction, as in *C*, fig 7, and phthalic acid may afford an example of this. Or, lastly, the curve may be indistinguishable from an ordinary vapour-pressure curve (*C*, fig. 8), as is the case with most substances.

[redacted]

[redacted]

§ 84. *Influence of one of the products of dissociation on the amount of dissociation.*—The results of HORSTMANN, MOITESSIER and ENGEL, and ISAMBERT have shown that the presence of excess of one of the products of dissociation diminishes the amount of dissociation. Their experiments were made by introducing a known quantity of one of the products of dissociation into a barometer-tube, in which the dissociable substance was being heated. WURTZ has also shown that the vapour-density of a dissociable compound is increased in presence of one of its components, which necessarily implies a decrease of dissociation. Now, it has been found by us from experiments with aldehyde ammonia and ammonium chloride that it is immaterial how pressure is raised in determining temperatures of volatilization; but the two cases are very different. In the former the gas in excess is mixed with, and acts on the vapour evolved from the dissociable body, while in the latter it is a question of the action on the solid of the gas introduced, since after the component vapours have left the surface of the solid, any action on them would have no influence on the solid. It appears most likely that the solid is always surrounded by its own vapour, so that it is doubtful whether the introduced gas ever comes in contact with the solid at all.

§85. *Difference of behaviour of dissociable solids from dissociable liquids when evaporating from a free surface.*—So long as the body is solid the residue has always its original composition; but a liquid separates into its components, the more volatile passing over first. This was found to be the case with chloral hydrate and with phthalic and succinic acids, and no doubt holds good with others. It amounts to a proof that the solid substance, in volatilizing, does not pass through the state of liquid. It would also show that a solid, so long as it remains a solid, cannot dissociate; while a liquid may undergo increased dissociation with rise of temperature, thus forming a mixture from which the more volatile constituent separates first.

§86. We have shown in the preceding pages that there is no essential difference, in certain cases of dissociation, between the behaviour of dissociating and evaporating bodies; but in others, where a deeper chemical change may be supposed to occur, an essential difference exists, as shown by a comparison of the curves representing, on the one hand, temperatures of volatilization under different pressures, and, on the other. vapour-pressures, or pressures of dissociation, at different temperatures. The precise nature of this difference is as yet unexplainable, in our present state of ignorance of the molecular and atomic constitution of chemical substances.

III. *On Evaporation and Dissociation.*—Part II. *A Study of the Thermal Properties of Alcohol.*

By William Ramsay, *Ph.D., and* Sydney Young, *D.Sc.*

Communicated by Professor G. G. Stokes, *Sec.R.S.*

Received April 18,—Read May 7, 1885.

[Plates 3–7.]

1. The density of gases is found to increase as the temperature falls towards their condensing point. This may be explained by one of two theories:—

(1) That complex gaseous molecules are formed in increasing numbers as the temperature falls; these complex molecules consisting of congeries of the simpler molecules known to exist in gases (see Playfair and Wanklyn, Trans. Roy. Soc. Edin., xxii., (3), p. 441, and 'Annalen,' 122, p. 245; also Naumann, 'Annalen,' 155, p. 325, and 'Thermochemie,' pp. 86 *et seq.*).

(2) That mutual attraction of the molecules, caused by their greater proximity, comes into play, and reduces their mean distance from each other.

The second of these hypotheses involves a deviation from Avogadro's law; while the first does not.

Similarly, with those substances in which dissociation takes place in the gaseous state, the density of the mixture of gases increases with fall of temperature, and this is doubtless caused by the increase in number of compound molecules. That this is the case with nitrogen peroxide can hardly be questioned, from the different physical properties of the gas under different conditions of temperature; and the phenomenon is also well seen in the case of tertiary amyl bromide.

It may be pointed out that both these causes may operate at the same time. It has occurred to us that light may be thrown on this question by a study of the thermal properties of three representative compounds:—

(1) What may be called a normal substance; *i.e.*, a substance in which no chemical dissociation is generally supposed to occur. Ethyl alcohol has been chosen as a representative of such a type.

(2) A substance the vapour-density of which shows marked abnormality, and which is suspected by many chemists of forming complex molecular groups. It is generally supposed that acetic acid, $C_2H_4O_2$, tends to form double molecules of the formula $C_4H_8O_4$, and that its abnormal vapour-density is to be explained on this hypothesis. Hence we have chosen it as a subject of experiment.

(3) It is hoped that it may be possible to effect a similar investigation of a sub-

stance which undoubtedly dissociates into dissimilar molecules, or the dissociation of which is undoubted from some change in its physical properties.

2. Such a study as we propose involves the determination, within the largest possible range of temperature, of the expansion of the liquid and of its compressibility; of the density of the vapour when unsaturated as well as when in contact with its liquid; and of the heat absorbed in producing change of state from liquid to gas.

We have already accumulated a number of data dealing with a portion of this problem; and as they are necessarily very voluminous, we deem it advisable to publish those bearing on the thermal constants of alcohol.

3. It is proposed to reserve until later a detailed description of the apparatus with which this research was executed. It will be sufficient here to state that it is a modification of ANDREWS' apparatus, provided with two air-gauges, one for measuring low, and the other for measuring high pressures. The temperature of each gauge was accurately known, for they were jacketed with running water in which a thermometer was immersed.

These gauges were graduated in millimetres and calibrated by weighing with mercury, and were filled with air dried with phosphorus pentoxide.

In calculating pressure, the following data were required:—

(1) The temperature and pressure of the air when the gauge was filled.

(2) The temperature of the air when readings were taken.

(3) The coefficient of compressibility of dry air, taking into account the deviation from BOYLE's law, as determined by AMAGAT, 'Comptes Rendus,' 99, p. 1153.

(4) The error of the gauges, corrected by calibration.

(5) The difference in height of the columns of mercury in the gauges and in the tube containing the liquid.

(6) The vapour-pressure of mercury in the experimental tube. At the highest temperature employed, 246°, it amounts to 68 mms., or about $\frac{1}{800}$th of the total pressure measured. For this, in many cases, we have applied no correction, for it is doubtful whether the mercury can give off vapour when its surface is covered by a long column of liquid. From experiments on the vapour-pressure of bromo-naphthalene at 237°, at which the vapour-pressure of mercury is 55 mms., it was noticed that a considerable time was required for the vapour to rise through a comparatively short column of liquid bromo-naphthalene. It is, therefore, probable that the full pressure of mercury vapour was not exercised: and the possible error is reduced below the experimental error of reading at such high pressures; but in the case of unsaturated vapour-densities, this correction was introduced.

4. The experimental tube, containing the alcohol, confined by mercury, was 200 mms. long, and was graduated in millimetres, and calibrated by weighing with mercury. It was made of lead-glass barometer-tube, with an internal diameter of about 2 mms. The coefficent of expansion of this glass was determined between 30° and 100°, and was found to be 0·0000257 per degree. In correcting for the meniscus of the mercury, the meniscus was regarded as a hemisphere.

A similar correction was made for the surface of the alcohol, no apparent change taking place until its temperature was raised to within a few degrees of its critical point. At those temperatures it was found that the error was inappreciable.

The experimental tube was heated by the vapours of pure liquids, boiling under pressures which could be varied at will. The vapour-pressures of these liquids have been accurately determined, temperature being measured with a mercury thermometer. Several measurements were carried out with an air-thermometer, and the necessary corrections were applied to reduce the readings of the mercurial thermometers used to those of an air-thermometer. The details of this investigation have been given in the Trans. Chem. Soc., 1886, p. 37; the results which are there published constitute a guarantee of the accuracy of the determination of temperature. We can state with confidence that at the highest temperature employed (246°) the absolute error does not amount to two or three-tenths of a degree; and the temperature can be altered with certainty through 0·05° by alteration of the pressure under which the liquid is boiling. This is, we believe, the only method by which a long tube can be uniformly heated; and by which the temperature can be easily and quickly altered. All the temperatures given are, therefore, those of an air-thermometer.

5. It is unnecessary to give details as regards reading, calibration, &c., for all our results. But as it may help to explain our method of procedure, one instance shall be given, and the method may be held to apply to all the other results.

The temperature on an air-thermometer at which aniline boils at an observed pressure of 703·2 mms., the temperature of the gauge being 14° (equivalent to 701·5 mms. at 0°), is 181·4°. At this temperature, the following readings were made:— Reading in experimental tube of upper surface of mercury, 210. Reading of upper surface of liquid, 139·7. Corresponding volumes corrected for meniscus: volume of liquid plus gas =0·65974 cc.; volume of gas =0·39591 cc. Add correction for expansion of glass; for higher volume, 0·00309; for lower volume, 0·00186. Corrected volumes =(1) 0·66283; (2) 0·39777 cc. Volume of liquid =0·26506 cc.; volume of gas =0·39777 cc. The volume was subsequently reduced, until only a minute bubble of vapour was left uncondensed. It was thus made certain that the liquid, as such, was not being compressed. The corrected volume was then found to be 0·28706 cc. The weight of the liquid in the tube was 0·17083 grm.; this latter number was found from several readings of the volume at known low temperatures, and the known specific gravity of alcohol at those temperatures.

The specific gravity of alcohol under pressure corresponding to that of its own vapour at 181·4°=0·17083/0·28706=0·5951. From this number is deduced the weight of the liquid (vol.) 0·26506 × (sp. gr.) 0·5951=0·15774 grm. The weight of the vapour=total weight−weight of liquid=0·17083−0·15774=0·01309 grm.

The weight of 1 cc. of vapour therefore equals its weight divided by its volume =0·01309 grm./0·39777 cc. =0·0329 grm.

Vapour density:—Weight of 1 cc. H at 181·4° and 15,163 mms. pressure =0·001074. Hence 0·0329/0·001074=30·65.

Pressure :—Reading on high-pressure gauge, 199·35. Temperature of gauge, 12·7°. Ratio of total volume of gauge tube to that of compressed air, the correction for the meniscus of the mercury in the gauge being applied, 20·008 : 1. Ratio corrected for temperature and pressure and for temperature at which gauge was filled =20·003 atmospheres =15,202−115*=15,087 mms. Add difference in heights of mercury in gauge and in experimental tube =76 mms., 15,087+76=15,163 mms. From this example an idea may be gathered as to the methods of reduction employed, and of the corrections introduced.

6. We now proceed to give results corrected by the method above explained.

PRESSURES of Vapour.

Vapour used as jacket.	T.	Number of observations.	Mean pressure in mms.
Chlorobenzene	89·85°	4	1,188
"	110·0	3	2,356
"	130·05	3	4,344
Bromobenzene	130·10	3	4,309
"	140·25	6	5,701
Methyl salicylate	150·0	3	7,353
Bromobenzene	150·65	6	7,400
Aniline	151·40	3	7,605
"	160·25	4	9,334
Methyl salicylate	161·0	3	9,647
Aniline	161·6	6	9,775
Methyl salicylate	171·0	3	12,170
Aniline	171·75	5	12,288
Methyl salicylate	180·95	3	15,078
Aniline	181·4	6	15,184
Methyl salicylate	189·8	4	18,102
Bromonaphthalene	199·3	3	21,851
Methyl salicylate	200·0	4	22,167
Bromonaphthalene	209·75	3	26,639
Methyl salicylate	210·05	4	26,894
Bromonaphthalene	219·9	3	31,990
"	219·9	3	31,967
Methyl salicylate	220·45	4	32,425
Bromonaphthalene	225·05	4	34,972
"	230·35	5	38,416
"	232·6	5	39,821
"	234·7	5	41,485
"	235·85	5	42,186
"	236·8	5	42,864
"	237·95	5	43,645
"	239·0	9	44,673
"	240·1	6	45,579
"	241·25	5	46,386
"	242·25	4	47,095
"	242·8	4	47,088
"	242·95	3	47,832
(Apparent critical point)	243·1	?	47,850

7. As it is impossible to distinguish between liquid and gas at the critical point, so it is impossible to give the vapour-pressure at the critical point. The pressures

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* Correction for divergence of dry air from BOYLE's law.

recorded will be given when treating of the compressibility of the liquid. They remained constant within the limits of reading during a considerable reduction of volume.

8. The vapour-pressure of alcohol has been measured by **Regnault** up to 150°. On examining his tabulated results by the method of differences, it was found that the third differences show irregularity at and above 110°; on taking the fourth differences minus quantities begin to appear. We find that our numbers to some extent confirm this peculiarity of **Regnault's** results. In order to calculate the pressures corresponding to even temperatures, the difference for 20°, *i.e.*, about 10° below and about 10° above the temperature requiring reduction was taken; and by dividing by the interval of temperature, the mean change for 1° was found. This was applied to reduce the pressure at the observed temperature to what it would be were the numbers representing temperature multiples of 10°. The error introduced by this somewhat crude method must necessarily be small, inasmuch as the required change of temperature seldom exceeds 1°.

From measurements, described in a later part of this paper, the vapour-pressure at 0° was found to be 12·24 mms. From this number, and from those at 60°, 120°, 180°, and 240°, constants for a formula of the type suggested by **Biot** were calculated. The formula is :—$\log p=a+b\alpha^t+c\beta^t$. The constants are :—$a=5{\cdot}0720301$; $\log b=\bar{2}{\cdot}6406131$; $\log c=0{\cdot}6050854$; $\log \alpha=0{\cdot}003377538$; $\log \beta=\bar{1}{\cdot}99682424$ (c is negative).

T.	Numbers given by Regnault.		Numbers found by R. and Y.	Δ.	Numbers from above formula.	Difference of 4th place.
° 0	12·70[*]	12·83[†]	12·24	0	12·24	..
10	24·23	24·30	23·77	+ ·05	23·73	..
20	44·46	44·48	44·00	+ ·03	43·97	2·132
30	78·52	78·49	78·06	− ·05	78·11	2·627
40	133·69	133·64	..	..	133·42	2·994
50	219·90	219·88	..	..	219·82	3·417
60	350·21	350·26	..	..	350·21	3·570
70	541·15	541·21	..	..	540·91	3·73
80	812·91	812·76	..	..	811·81	3·61
90	1189·30	1188·43	1194·3	+ 7·8	1186·5	3·46
100	1697·55	1694·92	..	..	1692·3	3·26
110	2367·64	2361·63	2356	− 3·9	2359·8	2·90
120	3231·73	3219·68	..	..	3223·0	2·72
130	4323·00	4301·04	4320	+ 1·3	4318·7	2·57
140	5674·59	5637·00	5666	− 20·6	5686·6	2·75
150	7318·40	7258·73	7326	− 42·7	7368·7	2·79
160	..	..	9366	− 43·9	9409·9	3·44
170	..	..	11856	− 2·0	11858	5·94
180	..	..	14763	− 1·0	14764	3·94
190	..	..	18178	− 7·0	18185	9·0
200	..	..	22164	− 18·0	22182	12·0
210	..	..	26821	− 4·0	26825	12·0
220	..	..	32097	− 99·8	32196	21·0
230	..	..	38176	−213	38389	..
240	..	..	45504	− 15	45519	..

[*] 'Mémoires de l'Institut,' vol. xxvi., p. 374.

[†] 'Comptes Rendus,' vol. l., 1860, p. 1067.

9. *Specific Gravities and Specific Volumes.*

In order to ascertain the specific gravity of alcohol, it was necessary to know the volumes at various temperatures, and the total weight of substance. As the weight was not the same throughout, losses having occurred through breakage, it was not possible to obtain the weight directly. It was, therefore, necessary to deduce the weight from the volume and the known specific gravity at low temperatures.

The results given by different observers are, however, not uniform. We quote some of these; in all cases comparison is made with water at 4° as unity.

	Sp. gr.	Sp. vol.
Pierre ('Annalen,' 56, p.142, and 'Annales,' 15, p. 325)	0·81510	1·2268
Kopp ('Annalen,' 64, p. 213)	0·80950	1·2351
Mendelejeff ('Annalen,' 119, p. 7)	0·80832	1·2371
Perkin (Chem. Soc. Journ., 45, p. 465)	0·80696	1·2392
Mendelejeff (Roscoe and Schorlemmer, vol. iii., pt. 1, p. 299)	0·80625	1·2403
Squibb (Chem. News, 51, p. 21)	0·80573	1·2411

In calculating our results, the number 1·2403 was taken; it will be seen that the mean of the last three results, which are probably the best, is 1·2402. The alcohol employed had been frequently distilled over lime, and was finally dried by distillation with a little sodium. It boiled with perfect constancy.

10. During these experiments, an accident occurred, by which we lost the first portion of alcohol; the tube was therefore refilled. We shall name the first portion A, and the second B, in giving data.

	T.	V.	Wt.	Mean.
A.	° 16·5	0·21557	0·17082	0·17083
	16·7	0·21564	0·17084	
B.	15·0	0·21954	0·17420	

11. In the following table, the pressure under which the liquid was measured, was in general the vapour-pressure corresponding to the temperature. The asterisked figures are corrected to this standard from observation on the compressibility.

A.	T.	Volume.	Sp. gr.	Sp. vol. $=\frac{1}{\text{sp. gr.}}$ = vol. of 1 grm.	Volume, $V_0=1·0$.
		cub. centims.			
	110°	0·24119	0·70606	1·4163	..
	130·05	0·25150	0·6792	1·4723	1·1871
	140·25	0·25821	0·6616	1·5115	1·2187
	150·65	0·26454	0·6458	1·5486	1·2486
	161·60	0·27038	0·6318	1·5828	1·2761
	171·75	0·27830	0·6138	1·6291	1·3135
	181·40	0·28706	0·5951	1·6804	1·3548
	189·80	0·29474	0·5796	1·7254	1·3911
	200·00	0·30671	0·5570	1·7954	1·4475
	210·05	0·32292	0·5290	1·8903	1·5241
	220·45	0·34572	0·4941	2·0238	..
*	,,	..	0·4943	2·0232	1·6312
	225·05	0·35731	0·4781	2·0917	1·6864
	230·35	0·37479	0·4558	2·1940	..
*	,,	..	0·4535	2·2051	..
	232·60	0·38482	0·4439	2·2527	..
*	,,	..	0·4420	2·2626	..
	234·70	0·39890	0·4282	2·3351	..
*	,,	..	0·4280	2·3367	..
	235·85	0·40449	0·4223	2·3678	..
*	,,	..	0·4214	2·3729	..
	236·80	0·41457	0·4121	2·4269	..
*	,,	..	0·4112	2·4317	..
	237·95	0·41906	0·4076	2·4531	..
*	,,	..	0·4055	2·4659	..
	239·0	0·42819	0·3989	2·5066	..
*	,,	..	0·3954	2·5291	..

B.	T.	Volume.	Sp. gr.	Sp. vol. (V. of 1 grm.)	Volume, $V_0=1·0$.	Mean of A and B volume, $V_0=1·0$.
		cub. centims.				
	160°·25	0·27523	0·6329	1·5800	1·2739	..
	230·35	0·38567	0·4517	2·2140	..	1·7814
	232·60	0·39539	0·4406	2·2698	..	1·8271
	234·70	0·40784	0·4271	2·3412	..	1·8858
	235·85	0·41382	0·4210	2·3755	..	1·9142
	236·80	0·42129	0·4135	2·4184	..	1·9551
	237·95	0·43188	0·4034	2·4792	..	1·9935
	239·00	0·44346	0·3928	2·5457	..	..
	239·00	0·44624	0·3904	2·5617	..	..
*	,,	..	0·3898	2·5654	..	2·0533
	240·10	0·46006	0·3786	2·6410	..	..
*	,,	..	0·3802	2·6303	..	..
	240·10	0·45481	0·3830	2·6108	2·1128	..
	241·25	0·47426	0·3673	2·7225	..	..
	241·25	0·47087	0·3699	2·7030	2·1871	..
	242·25	0·50610	0·3442	2·9053	..	..
	242·25	0·49528	0·3517	2·8432	2·2956	..
	242·80	0·52291	0·3331	3·0019	..	..
	242·80	0·51619	0·3375	2·9632	2·4046	..
	242·95	0·56026	0·3109	3·2162	2·5930	..

12. *Compressibility.*

The compressibility was measured by increasing the pressure, and after some time reading the volume of the liquid. It was noticed that heat was developed by compression, hence time was allowed for the heat to dissipate before reading. The following are the results:

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
110°	2,358	0·24119	1·4163	230·35°	38,914	0·38331	2·2004
"	13,432	0·23970	1·4076	"	39,722	0·37958	2·1790
"	38,065	0·23784	1·3967	"	41,156	0·37573	2·1569
130·05	4,344	0·25150	1·4723	"	42,695	0·37201	2·1355
"	6,720	0·25057	1·4668	"	44,464	0·36816	2·1134
"	14,694	0·24971	1·4618	"	46,647	0·36442	2·0919
"	21,268	0·24926	1·4591	"	48,591	0·36071	2·0707
"	38,055	0·24758	1·4493	"	50,675	0·35701	2·0494
140·25	5,760	0·25821	1·5115	"	53,522	0·35326	2·0279
"	6,707	0·25784	1·5094	"	55,264	0·35139	2·0265
"	8,643	0·25779	1·5091	232·60	40,143	0·38482	2·2527
"	13,634	0·25736	1·5065	"	41,360	0·37959	2·2220
"	22,088	0·25653	1·5017	"	46,650	0·36444	2·1334
"	39,331	0·25391	1·4864	"	61,536	0·34259	2·0054
150·65	7,460	0·26454	1·5486	232·60	39,918	0·39539	2·2698
"	15,198	0·26286	1·5387	"	40,963	0·39090	2·2440
"	21,900	0·26173	1·5321	"	41,758	0·38719	2·2226
"	38,993	0·26034	1·5240	"	42,906	0·38333	2·2005
160·25	9,190	0·27523	1·5800	"	43,949	0·37959	2·1790
"	20,828	0·27262	1·5650	"	45,590	0·37575	2·1570
"	37,058	0·27000	1·5499	"	47,037	0·37202	2·1356
"	61,037	0·26702	1·5328	"	48,851	0·36817	2·1135
161·60	9,804	0·27038	1·5828	"	51,433	0·36443	2·0920
"	21,977	0·26852	1·5719	"	53,441	0·36073	2·0708
"	39,130	0·26553	1·5544	"	55,905	0·35703	2·0496
171·75	12,366	0·27830	1·6291	234·70	41,571	0·39890	2·3351
"	22,090	0·27606	1·6160	"	46,614	0·37578	2·1997
"	39,158	0·27270	1·5964	"	61,749	0·34807	2·0376
"	64,235	0·26860	1·5724	234·70	41,566	0·40784	2·3412
181·40	11,465	0·28817	1·6869	"	42,379	0·40224	2·3091
"	15,149	0·28706	1·6804	"	43,022	0·39845	2·2873
"	38,545	0·28099	1·6449	"	43,902	0·39467	2·2656
"	63,482	0·27577	1·6143	"	44,696	0·39093	2·2442
189·80	18,011	0·29474	1·7254	"	45,837	0·38721	2·2228
"	63,769	0·28264	1·6545	"	46,958	0·38335	2·2006
200	22,207	0·30671	1·7954	"	48,084	0·37962	2·1792
"	63,838	0·29166	1·7074	"	49,631	0·37578	2·1571
210·05	26,976	0·32292	1·8903	"	51,584	0·37205	2·1357
"	61,911	0·30429	1·7813	"	52,861	0·36820	2·1137
220·45	32,336	0·34572	2·0238	"	55,631	0·36446	2·0922
"	62,157	0·31950	1·8703	235·85	42,278	0·40449	2·3678
225·05	34,932	0·35731	2·0917	"	46,685	0·38075	2·2288
"	46,548	0·33980	1·9891	"	61,836	0·35070	2·0530
"	61,664	0·32695	1·9139	235·85	42,309	0·41382	2·3755
230·35	38,802	0·37479	2·1940	"	42,942	0·40971	2·3520
"	46,430	0·35524	2·0795	"	43,496	0·40599	2·3306
"	61,524	0·33810	1·9792	"	44,170	0·40225	2·3092
230·35	38,386	0·38567	2·2140	"	44,641	0·39846	2·2873

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
°				°			
235·85	45,228	0·39468	2·2657	240·1	45,567	0·46006	2·6410
,,	46,316	0·39094	2·2442	,,	52,511	0·39695	2·2787
,,	47,356	0·38722	2·2228	,,	61,065	0·37420	2·1481
,,	48,834	0·38336	2·2007	240·1	45,347	0·45481	2·6108
,,	50,032	0·37963	2·1793	,,	45,861	0·44720	2·5671
,,	51,761	0·37579	2·1572	,,	46,225	0·43973	2·5243
,,	53,535	0·37206	2·1358	,,	46,662	0·43240	2·4822
,,	55,309	0·36821	2·1137	,,	47,366	0·42475	2·4383
236·80	42,951	0·41457	2·4269	,,	48,295	0·41721	2·3950
,,	46,703	0·38860	2·2748	,,	49,566	0·40975	2·3522
,,	61,858	0·35368	2·0704	,,	51,194	0·40229	2·3093
236·8	42,888	0·42129	2·4184	,,	52,783	0·39472	2·2659
,,	43,421	0·41718	2·3948	,,	55,540	0·38726	2·2231
,,	43,752	0·41346	2·3734	241·25	46,452	0·47426	2·7225
,,	44,202	0·40972	2·3520	,,	52,641	0·40492	2·3245
,,	44,892	0·40600	2·3307	,,	61,218	0·37899	2·1756
,,	45,722	0·40226	2·3092	241·25	46,107	0·47087	2·7030
,,	46,333	0·39847	2·2874	,,	46,230	0·46227	2·6537
,,	47,179	0·39469	2·2657	,,	46,476	0·45482	2·6109
,,	48,025	0·39095	2·2442	,,	46,863	0·44721	2·5672
,,	49,125	0·38723	2·2229	,,	47,369	0·43974	2·5244
,,	50,435	0·38337	2·2007	,,	47,767	0·43241	2·4823
,,	51,973	0·37964	2·1793	,,	48,655	0·42476	2·4383
,,	53,433	0·37580	2·1573	,,	49,713	0·41722	2·3951
,,	55,349	0·37207	2·1358	,,	50,898	0·40976	2·3522
237·95	43,840	0·41906	2·4531	,,	52,785	0·40230	2·3094
,,	46,724	0·39507	2·3127	,,	54,739	0·39473	2·2659
,,	62,881	0·35704	2·0901	,,	55,716	0·39099	2·2445
237·95	43,742	0·43188	2·4792	242·25	47,137	0·50610	2·9053
,,	43,962	0·42846	2·4596	,,	52,498	0·41685	2·3929
,,	44,089	0·42473	2·4381	,,	61,025	0·38342	2·2010
,,	44,527	0·42092	2·4163	242·25	47,000	0·49528	2·8432
,,	45,119	0·41719	2·3949	,,	47,066	0·48849	2·8042
,,	45,714	0·41347	2·3735	,,	47,257	0·47722	2·7395
,,	46,318	0·40973	2·3521	,,	47,644	0·46603	2·6752
,,	46,960	0·40601	2·3307	,,	48,173	0·45483	2·6110
,,	47,610	0·40227	2·3092	,,	48,723	0·44349	2·5453
,,	48,274	0·39848	2·2875	,,	49,716	0·43242	2·4823
,,	49,395	0·39470	2·2658	,,	51,048	0·42096	2·4165
,,	50,419	0·39096	2·2443	,,	52,943	0·40977	2·3523
,,	51,643	0·38724	2·2230	,,	55,717	0·39852	2·2877
,,	52,922	0·38338	2·2008	242·60	47,282	0·52291	3·0019
,,	54,445	0·37965	2·1794	,,	47,528	0·49603	2·8475
,,	56,054	0·37580	2·1573	,,	47,795	0·47723	2·7396
239·0	44,774	0·42819	2·5066	,,	48,322	0·45857	2·6324
,,	46,724	0·40619	2·3778	,,	49,588	0·43976	2·5245
,,	61,882	0·36078	2·1119	,,	51,526	0·42097	2·4166
239·0	44,978	0·44624	2·5617	,,	55,216	0·40231	2·3095
,,	52,318	0·39097	2·2444	243·10	47,631	0·54458	3·1262
,,	60,958	0·37158	2·1330	,,	47,669	0·53336	3·0618
239·0	44,665	0·44346	2·5457	,,	47,706	0·51469	2·9546
,,	44,776	0·43599	2·5028	,,	47,971	0·49603	2·8475
,,	45,359	0·42847	2·4596	,,	48,298	0·47723	2·7396
,,	46,220	0·42093	2·4164	,,	49,203	0·45857	2·6324
,,	47,240	0·41348	2·3736	,,	50,284	0·43976	2·5245
,,	48,436	0·40602	2·3308	,,	52,286	0·42097	2·4166
,,	50,133	0·39849	2·2875	,,	56,745	0·40231	2·3095
,,	51,976	0·39097	2·2443	243·1	47,127	0·92225	5·2942
,,	54,820	0·38339	2·2008	,,	47,178	0·88520	5·0815

T.	P.	V. in ccs.	V. of 1 gram.	T.	P.	V. in ccs.	V. of 1 gram.
243·10°	47,242	0·86672	4·9754	243·55°	61,121	0·38803	2·2275
"	47,297	0·84818	4·8690	244·35	48,278	0·88522	5·0816
"	47,360	0·82964	4·7626	"	48,269	0·84820	4·8691
"	47,423	0·81111	4·6562	"	48,386	0·81096	4·6553
"	47,471	0·79268	4·5504	"	48,627	0·77421	4·4444
"	47,528	0·77419	4·4443	"	48,935	0·73760	4·2342
"	47,523	0·75589	4·3392	"	49,054	0·70118	4·0251
"	47,587	0·73758	4·2341	"	49,105	0·66387	3·8104
"	47,653	0·79198	4·1258	"	49,215	0·62653	3·5966
"	47,659	0·70086	4·0233	"	49,205	0·58937	3·3833
"	47,654	0·66228	3·9166	"	49,195	0·55205	3·1691
"	47,649	0·66385	3·8108	"	49,316	0·51472	2·9548
"	47,644	0·64516	3·7026	"	50,088	0·47724	2·7396
"	47,639	0·62651	3·5965	"	52,452	0·43976	2·5251
"	47,634	0·60795	3·4900	"	61,144	0·39585	2·2724
"	47,629	0·58937	3·3833	246·0	49,483	0·88526	5·0818
"	47,624	0·57070	3·2761	"	49,673	0·84824	4·8693
"	47,620	0·55204	3·1690	"	49,791	0·81100	4·6555
"	47,614	0·53336	3·0618	"	49,917	0·77425	4·4446
"	47,679	0·51469	2·9546	"	49,977	0·73763	4·2344
"	47,813	0·49603	2·8475	"	50,030	0·70121	4·0253
"	48,215	0·48097	2·7610	"	50,020	0·66390	3·8111
243·55	48,148	0·88520	5·0815	"	50,010	0·62656	3·5968
"	48,131	0·81094	4·6552	"	50,268	0·58941	3·3835
"	48,159	0·73758	4·2341	"	50,668	0·55208	3·1692
"	48,395	0·66385	3·8109	"	50,934	0·51474	2·9549
"	48,433	0·58937	3·3833	"	52,042	0·47727	2·7397
"	48,476	0·51471	2·9547	"	54,607	0·43979	2·5246
"	48,915	0·47723	2·7113	"	61,007	0·40152	2·3049
"	51,216	0·43976	2·5245				

The graphic representation of these numbers shows that the compressibility at low temperatures is nearly constant through a large range of pressure; but at high temperatures it varies, decreasing rapidly as pressure rises, and near the critical point, as observed by ANDREWS, the liquid is much more compressible than a gas.

13. By plotting these results in curves, we are enabled to give the volumes occupied by liquid alcohol at constant pressures, with variation of temperature. To do so, however, required a somewhat tedious process. The actual results were plotted on curve paper, and by means of engineers' curves (circles of different radii), lines were drawn, occupying as nearly as could be judged a mean position among the observed points. From these curves the volumes for certain definite pressures were read off, intervals of 5000 mms. at low temperatures, and 2500 or 1250 mms. at high temperatures being chosen. From these numbers fresh curves were constructed, showing relations between temperature and volume for a series of pressures. These curves were also smoothed, and the results obtained by their means retransferred to the first set of curves. The curves published in Plate 3 show these doubly-smoothed curves, and the actual observations are also shown by circles, which will enable the amount of error to be estimated. The temperatures of the isothermals are written

on the horizontal lines which represent change of volume without increase of pressure, where vapour in contact with liquid is being condensed.

14. The temperatures given are those read directly, with two exceptions, viz., 242·8° was altered to 242·6°, and 243·25° was altered to 243·55°. The reason for this alteration was that in drawing the isobaric curves, deduced from the isothermals, the observed points at those temperatures differed from the curve in every case by the same amount. This error is really a very small one at such high temperatures, and may depend on some mistake in reading the pressure under which the bromonaphthalene used as a jacket was boiling.

It is to be remarked that by this double method of smoothing any great irregularity of temperature would at once be detected; this is shown by the corrections above referred to.

15. From the isobaric curves we give results deduced for definite intervals of temperature and pressure.

T.	5000 mms.	10,000.	15,000.	20,000.	25,000.	30,000.	35,000.	40,000.	42,500.	45,000.	47,500.	50,000.	52,500.	55,000.	57,500.	60,000.	62,500.
110	1·414	1·411	1·408	1·405	1·402	1·400	1·399	1·398	..	1·396	..	1·395	..	1·394	..	1·393	..
120	1·441	1·437	1·433	1·430	1·428	1·426	1·424	1·421	..	1·420	..	1·418	..	1·416	..	1·413	..
130	1·470	1·466	1·462	1·459	1·456	1·452	1·450	1·449	..	1·446	..	1·444	..	1·442	..	1·441	..
140	..	1·499	1·494	1·490	1·486	1·483	1·480	1·478	..	1·477	..	1·472	..	1·470	..	1·468	..
150	..	1·536	1·530	1·524	1·519	1·517	1·512	1·510	..	1·508	..	1·504	..	1·501	..	1·500	..
160	..	1·577	1·569	1·562	1·558	1·554	1·550	1·547	..	1·542	..	1·540	..	1·537	..	1·534	..
170	..	..	1·616	1·607	1·600	1·597	1·591	1·588	..	1·582	..	1·580	..	1·576	..	1·572	..
180	..	..	1·666	1·660	1·653	1·647	1·642	1·636	..	1·631	..	1·625	..	1·620	..	1·615	..
190	..	..	..	1·724	1·714	1·706	1·699	1·690	..	1·681	..	1·676	..	1·669	..	1·661	..
200	..	..	..	..	1·790	1·779	1·767	1·755	..	1·745	..	1·736	..	1·727	..	1·719	..
210	..	..	..	..	..	1·869	1·850	1·834	1·828	1·820	1·813	1·809	1·801	1·797	1·791	1·788	1·781
215	..	..	..	..	..	..	1·909	1·882	1·872	1·863	1·857	1·850	1·842	1·837	1·831	1·827	1·820
220	..	..	..	..	..	..	1·982	1·946	1·930	1·919	1·908	1·898	1·890	1·881	1·877	1·870	1·862
225	..	..	..	..	..	..	2·092	2·039	2·015	1·998	1·979	1·963	1·950	1·939	1·930	1·920	1·911
230	..	..	..	..	..	..	..	2·163	2·129	2·099	2·072	2·050	2·029	2·009	1·998	1·982	1·970
232	..	..	..	..	..	..	..	2·240	2·191	2·150	2·120	2·090	2·067	2·041	2·027	2·010	1·999
234	..	..	..	..	..	..	..	..	2·265	2·210	2·171	2·135	2·104	2·078	2·059	2·040	2·025
236	..	..	..	..	..	..	..	..	..	2·290	2·232	2·188	2·150	2·117	2·097	2·073	2·053
238	..	..	..	..	..	..	..	..	..	2·400	2·311	2·250	2·203	2·161	2·140	2·110	2·088
240	..	..	..	..	..	..	..	..	..	..	2·428	2·328	2·268	2·214	2·189	2·156	2·131
242	..	..	..	..	..	..	..	..	..	..	..	2·441	2·351	2·284	2·248	2·208	2·176
244	..	..	..	..	..	..	..	..	..	..	..	..	2·493	2·380	2·325	2·270	2·222
246	..	..	..	..	..	..	..	..	..	..	..	..	..	2·497	2·418	2·341	2·280

16. A set of determinations have been made by Zuk (Z. Rusk. Chim. Obs., 13 (2), p. 239) of the volumes of alcohol under the critical pressure observed by Sajotcewsky of 62·1 atmospheres (=47,196 mms.). We are now in a position to compare our results with his. Zuk adopts the specific gravity 0·80614 at 0°, a number close to that adopted by us, 0·80625. The comparison is as follows:—

T.	$V_0=1$.	
	R. and Y.	Zuk.
124·3°	1·153	1·1667
132·5	1·170	1·1828
140·2	1·189	1·2004
150·6	1·216	1·2291
169·8	1·274	1·2914
181·0	1·317	1·3387
190·5	1·357	1·3815
200·5	1·406	1·4398
211·6	1·473	1·5228
218·5	1·524	1·5983

It is evident that there are considerable differences between the two sets of results. These are probably to be accounted for by differences in temperature. It should be remarked that Zuk employs as the temperature of the critical point 233·7°. The formula used by Zuk is one given by Avenarius, viz.:—

$$V=220{\cdot}59-50{\cdot}91\log(233{\cdot}7-t).$$

As this formula is entirely empirical, there is nothing to be gained by its use, although it appears to give an approximation to the found results.

17. We are now able to give the specific volumes and specific gravities of liquid alcohol at definite intervals of temperature and at pressures equal to the vapour-pressures at those temperatures. They are given in the following table. They are read from a smoothed curve representing individual observations of temperature and volume, and checked by means of the curves representing compressibility for known rise of pressure at constant temperature. In Plate 3, the observations shown by circles determine the direction of each curve. The curve connecting their terminals, which exhibits relations between the volume of the liquid, the temperatures, and the pressures equal to the vapour-pressures at those temperatures, was constructed by correcting the volumes when not read at the true vapour-pressures to the true volumes at those pressures. The curve was drawn through the points thus obtained, and it was seen that the points of intersection of these curves confirmed the position of points on a curve representing the relations between volumes and temperatures at the vapour-pressures corresponding to the temperatures. We would suggest the

name "orthobaric" as applicable to such a curve, and "orthothermic" to denote the curve representing relations between volumes and pressures at temperatures corresponding to the vapour-pressures of the substance.

18. It would be possible to obtain the volumes of 1 gram of the liquid at definite temperatures and at corresponding vapour-pressures directly from the "orthobaric" curve, or by constructing new isothermals, by means of the isobaric curves, for such temperatures and reading the points of intersection of such curves with the "orthothermic" curve. Since the results for the temperatures of observation were practically identical, it was judged sufficient to read them directly from the "orthobaric" curve.

19. The numbers thus read are as follows ;—

SPECIFIC Volumes [*] and Specific Gravities of Alcohol at Definite Temperatures, and at the Vapour-pressures corresponding to these Temperatures.

T.	Sp. v.	Sp. gr.	T.	Sp. v.	Sp. gr.
°			°		
110	1·417	0·7057	225	2·094	0·4775
120	1·444	0·6925	230	2·198	0·4550
130	1·473	0·6789	232	2·250	0·4444
140	1·508	0·6631	234	2·314	0·4292
150	1·541	0·6489	236	2·390	0·4184
160	1·580	0·6329	237	2·435	0·4107
170	1·622	0·6165	238	2·483	0·4027
180	1·671	0·5984	239	2·541	0·3935
190	1·7295	0·5782	240	2·614	0·3825
200	1·796	0·5568	241	2·699	0·3705
210	1·890	0·5291	242	2·820	0·3546
220	2·017	0·4958	242·5	2·925	0·3419

20. For the sake of comparison, we give HIRN'S ('Annales,' (4), 10, p. 32) and MENDELEJEFF'S (*loc. cit.*) numbers.

MENDELEJEFF . . $T=130{\cdot}9^\circ$ ($V_0=1$) ; 1·1895. Found (R. and Y.) 1·190.
HIRN . . . . . $T=150{\cdot}0^\circ$ ($V_0=1$) ; 1·24074. Found (R. and Y.) 1·243.

ZUK also, *loc. cit.*, gives numbers for the volumes of alcohol. These have already been considered.

Specific Volumes and Specific Gravities of Saturated Vapour of Alcohol.

21. It has been explained in § 5 how the volume of the saturated vapour was measured, and the various corrections introduced. We now proceed to give the experimental numbers.

---

[*] As some confusion has been introduced by the use of the phrase "specific volume" as synonymous with "atomic" or "molecular volume," it should here be stated that the expression is employed to denote the volume of 1 grm. of the substance.

In calculating the weight of 1 cub. centim. of saturated vapour, it has been pointed out, in § 5, that this constant depends on the specific gravity of the liquid. Now the specific gravity of the liquid may be taken, (1) as directly read, or (2) from the smoothed orthobaric curve. Both of these have been made use of, and the results are compared in the following table :—

T.	Weight of 1 cub. centim. vapour.		Weight of 1 cub. centim. of vapour smoothed by curve.	Vol. of 1 gram. of vapour.
	(1.)	(2.)	(3.)	
°	grms.	grms.		cub. centims.
110·0	0·00713	0·00728	0·00577 0·00650	173 154
130·05	0·01025	0·01041	0·01055 0·01090	94·8 91·7
140·25	0·01403	0·01370	0·01365 0·01370	73·3 73·0
150·65	0·01743	0·01743	0·01705	58·6
160·25	0·02278	0·02255	0·02090	47·8
161·6	0·01969	0·02044	0·02140	46·7
171·75	0·02608	0·02608	0·02615	38·2
181·4	0·03233	0·03135	0·03200	31·2
189·8	0·03882	0·03882	0·03860	25·9
200·0	0·04907	0·04916	0·04955	20·2
210·05	0·06578	0·06620	0·0655	15·3
220·45	0·08606	0·08676	0·0862	11·6
225·05	0·09711	0·09738	0·0977	10·2
230·35	0·11446	0·11431	0·1145	8·73
232·6	0·12324	0·12331	0·1235	8·10
234·7	0·13426	0·13434	0·13325	7·50
235·85	0·13870	0·13909	0·1394	7·17
236·8	0·14569	0·14554	0·1450	6·90
237·95	0·15184	0·15225	0·1529	6·54
239·0	0·16209 0·16092	0·16119 0·16080	0·1615	6·19
240·1	0·17271	0·17277	0·1727	5·79
241·25	0·18643	0·18719	0·1870	5·35
242·25	0·20294	0·20294	0·2050	4·88
242·6	0·22431	0·22522	0·2250	4·44

The chief differences in the numbers in these columns are at low temperatures, where a small alteration in the specific gravity of the liquid causes a large change in the weight of 1 cc. of saturated vapour.

22. From the data already given, the densities compared with hydrogen under similar conditions of temperature and pressure were calculated. In these calculations the data given in columns 1, 2, and 3 of the preceding table have been employed, and the corresponding vapour-densities are similarly numbered. The vapour-densities found were then plotted on a curve, and the 4th column shows the smoothed results.

Densities of Saturated Vapour (H=1).

T.	(1.)	(2.)	(3.)	(4.)
110·0°	36·0	36·7	29·1 32·8	29·5 32·8
130·05	29·6	29·9	30·4 31·5	29·5 31·5
140·25	31·6	30·9	30·7 30·9	29·5 30·7
150·65	30·3	30·3	29·6	29·45 30·0
160·25	32·85	32·55	30·15	29·45 29·6
161·6	27·2	28·2	29·5	29·35 29·5
171·75	29·3	29·3	29·4	29·4
181·4	30·0	29·1	29·7	29·8
189·8	30·8	30·8	30·65	30·7
200·0	32·6	32·6	32·9	33·1
210·05	36·7	36·9	36·55	36·4
220·45	40·75	41·05	40·85	40·85
225·05	43·1	43·2	43·3	43·4
230·35	46·7	46·7	46·7	46·85
232·6	48·8	48·8	48·9	48·9
234·7	51·2	51·2	50·8	50·9
235·85	52·15	52·25	52·35	52·35
236·8	54·0	53·8	53·7	53·8
237·95	55·4	55·55	55·75	55·55
239·0	57·9 57·5	57·6 57·4	57·7	57·7
240·1	60·55	60·55	60·55	60·55
241·25	64·3	64·6	64·5	64·5
242·25	69·1	69·1	69·8	69·8
242·6	76·45	76·75	76·65	76·65

23. It is evident, on inspection of this and the preceding table, that the results at lower temperatures are not nearly so accurate as those at higher. The cause of this is that an error in the specific gravity of the liquid, which would have almost no effect on the vapour-densities at higher temperatures exercises a serious influence, for it will be remembered that the weight of the vapour is deduced from the total weight of substance and the weight of the liquid, while the weight of the liquid is deduced from its specific gravity and its volume. As the difference between the total weight and the weight of the liquid is very small, the ratio of the error in the weight of the liquid, and therefore of the vapour, to the total weight of vapour is a large one.

24. The preceding table also shows that the vapour-density decreases very rapidly at first, and afterwards more and more slowly with fall of temperature, from the highest temperature to about 180°. Below that temperature the results were not certain enough to enable us to decide positively whether the density of the saturated vapour remains constant during a considerable fall of temperature or whether it begins to increase slowly. Determinations shall be described further on which elucidate this point. It is one of extreme importance, for an increase of vapour-density

would imply the probable formation of complex molecular groups; that this is the case with acetic acid vapour will be shown in a subsequent memoir.

25. In concluding this part of the subject we give a table taken from the curves, showing specific volumes, specific gravities, and vapour-densities at definite intervals of temperature.

SPECIFIC Gravity, Specific Volume, and Density of Saturated Vapour at definite Intervals of Temperature.

T.	Sp. gr.	Sp. vol.	V. dens.	T.	Sp. gr.	Sp. vol.	V. dens.
°		cub. centims.		°		cub. centims.	
110	0·00577	173	29·5	200	0·0495	20·2	33·1
	0·00650	154	32·8	210	0·0651	15·4	36·4
120	0·00800	125	29·5	220	0·0854	11·7	40·75
	0·00850	118	32·1	225	0·0976	10·25	43·4
130	0·0105	95·2	29·5	230	0·1135	8·81	46·7
	0·0108	92·6	31·4	232	0·1209	8·27	48·3
140	0·0135	74·1	29·5	234	0·1296	7·72	50·15
	0·0136	73·5	30·7	236	0·1401	7·14	52·5
150	0·0170	58·8	29·45	237	0·1463	6·83	53·9
			30·05	238	0·1532	6·53	55·65
160	0·0208	48·1	29·45	239	0·1615	6·19	57·7
			29·6	240	0·1715	5·83	60·2
170	0·0253	39·5	29·4	241	0·1835	5·45	63·5
180	0·0310	32·3	29·7	242	0·1990	5·02	67·3
190	0·0388	25·8	30·85	242·5	0·2164	4·62	74·25

The bracketed numbers express the limits between which these constants appeared to fall.

26. *Heats of Vaporisation of Alcohol.*

From the foregoing data it is possible to calculate the heats of vaporisation of alcohol by means of the formula

$$L=(s_1-s_2).\frac{t}{J}\frac{dp}{dt}.$$

L= Heat of vaporisation.
s_1 and s_2= Volumes of saturated vapour and liquid respectively.
t= Absolute temperature.
J= Mechanical equivalent of heat. =42500.
$\frac{dp}{dt}$= Rate of change of pressure, measured in grammes per square centimetre.

27. This rate of change was ascertained from the vapour-pressures of alcohol, calculated by BIOT'S formula, two points being chosen, 0·1° above and 0·1° below the temperature required, and the difference between these pressures was multiplied by 5. From 231° to 239° inclusive the values were read from a curve constructed to show relations of $\frac{dp}{dt}$ to temperature; the number at 240° is calculated, but at 241°, 242°, and 242·5° the curve was again employed. The results are given in the following table:—

VALUES of $\frac{dp}{dt}$ for definite Temperatures.

T.	$\frac{dp}{dt}$.	T.	$\frac{dp}{dt}$	T.	$\frac{dp}{dt}$
0°	0·840	130°	122·45	232°	684·0
10	1·516	140	151·75	233	692·5
20	2·616	150	185·41	234	701·0
30	4·332	160	223·72	235	710·5
40	6·898	170	266·75	236	721·0
50	10·575	180	315·45	237	731·0
60	15·750	190	369·70	238	741·0
70	22·75	200	430·80	239	751·5
80	31·85	210	499·3	240	763·7
90	43·61	220	576·6	241	774·5
100	58·17	225	620·0	242	785·0
110	75·95	230	664·0	245·5	790·0
120	97·33	231	674·5		

28. VALUES of L.

T (Cent.).	T (Abs.).	$\frac{T}{J}$*	$\frac{dp}{dt}$†	$s_1 - s_2$.	L in calorics.
110°	383°	0·00901	103·26	171·6 152·6	159·67 141·99
120	393	0·00925	132·33	123·6 116·6	157·82 142·67
130	403	0·00948	166·48	93·7 91·1	147·92 143·82
140	413	0·00972	206·32	72·6 72·0	145·59 144·39
150	423	0·00995	252·08	57·25	143·6
160	433	0·01019	304·17	46·5	144·1
170	443	0·01042	362·67	37·9	143·3
180	453	0·01066	428·9	30·6	139·9
190	463	0·01089	502·65	24·1	132·0
200	473	0·01113	585·7	18·4	119·9
210	483	0·01136	678·85	13·5	104·15
220	493	0·01160	783·9	9·7	88·2
225	498	0·01172	842·9	8·16	80·6
230	503	0·01184	902·8	6·61	70·6
232	505	0·01188	930·0	6·02	66·6
234	507	0·01193	953·1	5·41	61·5
236	509	0·01198	979·4	4·75	55·7
237	510	0·01200	993·9	4·40	52·5
238	511	0·01202	1007·5	4·05	49·0
239	512	0·01205	1021·8	3·65	47·5
240	513	0·01207	1038·3	3·22	40·3
241	514	0·01209	1053·0	2·75	35·0
242	515	0·01212	1067·3	2·20	28·4
242·5	515·5	0·01213	1074·1	1·695	22·1

(For correct values below number 210° refer to § 40.)

* The value of J was taken as 42500.

† In grammes per square centimetre.

29. It will be seen from these numbers that the values of L increase regularly to 180° with fall of temperature. They then appear to remain approximately constant. It is at this temperature also that the vapour-densities become uncertain, and show a tendency to rise. From the nature of the equation used to obtain the values of L any discrepancy in the vapour-densities will affect the values of L. At temperatures below 180°, as explained in § 23, the error introduced becomes considerable, and the experimental results are evidently no longer trustworthy. But above this temperature the ratios of the specific gravity of the liquid to that of the gas becomes sufficiently small to give accurate results; and the accuracy is confirmed by the regularity of the deduced curve.

30. There are already data as regards the heat of vaporisation of alcohol. **Andrews** (Chem. Soc. Journ., I., p. 27) gives the value of L for 77·9°, under a pressure of 760 mms., as 202·4 cal. **Favre** and **Silbermann** ('Annales' (3), 37, p. 465) give at the boiling-point under normal pressure 208·92 cal. **Regnault** ('Mémoires de l'Institut,' xxvi., pp. 819 and 262) gives a number of values of the total heats, from which the heats of vaporisation may be calculated by subtracting the specific heats of the liquid, calculated according to the formula given by him:—

$$\log \text{Sp. Ht.} = \bar{1}{\cdot}7384166 + \bar{3}{\cdot}0499296t + \bar{6}{\cdot}3436027t^2.$$

These numbers are as follows, and we append the volumes of saturated vapour and the resulting vapour-densities calculated from his numbers. They are shown graphically on the accompanying curve in Plate 4 (1):—

T.	Total heat.	Latent heat.	$\frac{dp}{dt}$	Vol. of 1 gram. of vapour.	Vap. density.
°	centims.				
0	236·5	236·5	0·854	33,435	21·08
10	244·4	238·8	1·525	17,297	21·00
20	252·0	240·6	2·565	10,008	20·48
30	258·0	240·5	4·23	5,866·8	20·45
40	262·0	238·2	6·82	3,489	20·865
50	264·0	233·5	10·635	2,126	21·50
60	265·0	227·6	15·975	1,338	22·11
70	265·2	220·6	23·14	877·5	22·26
80	265·2	213·1	32·43	583·0	23·16
90	266·0	206·0	44·19	402·6	23·57
100	267·3	199·1	58·73	285·4	23·94
110	269·6	192·9	75·60	209·5	24·01
120	272·5	186·8	97·0	154·5	24·47
130	276·0	181·0	123·35	119·7	24·22
140	280·5	175·8	152·05	89·02	25·42
150	285·3	170·5	186·5	69·11	26·01

As alcohol cannot without dissociating possess a vapour-density less than 23, the numbers below 80° are manifestly wrong.

Andrews' measurement gives a vapour-density of 23·51; and **Favre** and **Silber-**

MANN'S, 23·25; both of which agree well with our results. In these calculations our values of $\frac{dp}{dt}$ were employed.

31. HERWIG gives a formula by which the volume of 1 gram. of saturated vapour of various liquids may be calculated from the known value of PV when constant. This formula is

$$v_1 = \frac{v}{s} = \frac{PV}{0\cdot0595\sqrt{a+t.ps}}$$

Where v_1 is the volume of 1 gram; s the mass of substance; a, 273; t, temperature centigrade; and p, vapour-pressure at temperature t. Although this formula does not hold in the least at high temperatures, we give the results for alcohol calculated by HERWIG, at temperatures within the limits of which HERWIG states that his law holds good. (HERWIG states that the alcohol he used contained a trace of water.)

T.	P. (HERWIG)	v_1	$\frac{dp}{dt}$ (from REGNAULT)	L.	V.D.
23°	50·23	7977·9	2·99	225·85	22·97
30·5	77·58	5237·9	4·34	219·15	23·23
36·4	108·0	3798·4	5·80	216·4	23·46
41·9	144·7	2828·9	7·46	211·06	23·93
47·8	196·5	2125·0	9·68	209·55	23·90
57·8	315·8	1342·7	14·52	204·72	24·28
62·9	396·83	1076·6	17·81	204·39	24·48
69·9	537·63	802·4	22·98	200·55	24·76

If the vapour-densities were continued to lower temperatures they would manifestly fall below the lowest possible. Had our values of $\frac{dp}{dt}$ been substituted for those of REGNAULT, the discrepancy would have been even greater.

The numbers of ANDREWS, and of FAVRE and SILBERMANN, are fairly concordant, and appear to indicate a vapour-density of 23·25 to 23·5 at normal pressure; and it will be seen that a continuation of the curve obtained by us might hit this number at 78·4°.

It appeared desirable to confirm this view by further experiments in which different methods were employed.

32. *Densities of Unsaturated and Saturated Alcohol Vapour.*

For higher temperatures the process was essentially the same as that already described. A much smaller amount of alcohol was used, so that it was possible to convert it into gas, and to increase volume until its density became normal at a high temperature. Three sets of experiments were made. In the first too large an amount of alcohol was taken to enable the vapour to acquire normal density, even with the largest volume which could be given. The volume of the liquid was therefore measured at 220° and 225°, and its weight was calculated from the data obtained, and from the determinations of the specific gravity of alcohol which have already been described. In the second and third series the density was normal under the greatest volumes given, for the product of pressure into volume remained constant during change of volume.

SERIES I.

Weight of Substance.

I.	Volume at 220°	0·04323 cc.
	Sp. Gr.	0·4958.
	Weight	0·02143 gram.
II.	Volume at 225°	0·04514 cc.
	Sp. Gr.	0·4775.
	Weight	0·02155 gram. Mean, 0·02149.

T.	Volume.	Sp. vol. (vol. of 1 grm.)	P. mms.	P. V.	Vapour density.
220°	0·88473	41·27	14,181	12,548	26·23
,,	0·84773	39·54	14,714	12,476	26·39
,,	0·81051	37·80	15,238	12,352	26·66
,,	0·77379	36·09	15,869	12,278	26·81
,,	0·73719	34·38	16,505	12,170	27·05
,,	0·70211	32·75	17,188	12,069	27·27
,,	0·66350	30·95	17,958	11,917	27·63
,,	0·62618	29·21	18,776	11,757	28·00
,,	0·58901	27·47	19,670	11,585	28·42
,,	0·55175	25·73	20,635	11,387	28·91
,,	0·51441	23·99	21,679	11,152	29·53
,,	0·47697	22·25	22,813	10,882	30·26
,,	0·43953	20·50	24,140	10,610	31·04
,,	0·41098	18·75	25,560	10,275	32·06
,,	0·36433	16·99	27,004	9,840	33·48
,,	0·32709	15·26	28,656	9,372	35·14
,,	0·30880	14·40	29,408	9,080	37·29
,,	0·29107	13·57	30,278	8,813	37·37
,,	0·27268	12·72	31,182	8,503	38·73
,,	0·26151	12·20	31,861	8,332	39·53
,,	0·25140	11·85	32,153	8,170	40·31
,,	0·24668	11·51	32,162	7,934	Liquid present.
,,	0·23549	10·98	32,188	7,580	Liquid present.
,,	0·21687	10·11	32,183	6,979	Liquid present.

Series II.

33. A quantity of the alcohol was removed and a fresh set of determinations made at 220°. A curve was then constructed from the results of Series I., showing relation between volume and pressure; the volumes on this curve corresponding to the pressure on the second series were then read, and the ratios between the volumes in the two series at the same pressures were determined. By this method the weight of the alcohol used in Series II. was found to be 0·004751 grm. It will be seen that with this smaller quantity of substance the vapour-density at the higher temperatures and largest volumes becomes constant at 23, and this affords sufficient confirmation of the correctness of the weight given.

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
120°	0·88243	185·7	2725	2405	24·13
,,	0·84553	178·0	2826	2390	24·28
,,	0·80841	170·2	2942	2379	24·40
,,	0·77177	162·4	3061	2363	24·55
,,	0·75353	158·6	3117	2350	24·69
,,	0·74619	157·1	3142	2346	24·73
,,	0·73894	155·5	3167	2342	24·78
,,	0·73528	154·8	3176	2337	24·83
,,	0·73156	154·0	3185	2326	24·94
130	0·84575	178·0	2930	2478	24·01
,,	0·69884	147·1	3479	2433	24·45
,,	0·62471	131·5	3838	2399	24·81
,,	0·58762	123·7	4037	2374	25·08
,,	0·57273	120·6	4117	2360	25·22
,,	0·56529	119·0	4168	2357	25·24
,,	0·55785	117·4	4220	2355	25·27
,,	0·55414	116·6	4244	2352	25·29
,,	0·55045	115·9	4261	2346	25·36
,,	0·54668	115·1	4279	2340	25·43
140	0·84598	178·1	3012	2549	23·92
,,	0·73567	154·8	3445	2536	24·05
,,	0·62489	131·5	3978	2487	24·52
,,	0·51335	108·0	4749	2439	25·01
,,	0·43862	92·32	5428	2381	25·60
,,	0·42740	89·96	5533	2365	25·78
,,	0·41990	88·38	5606	2355	25·90
,,	0·41615	87·59	5653	2353	25·92
150	0·84618	178·0	3127	2646	23·60
,,	0·73583	155·0	3567	2625	23·80
,,	0·62503	131·5	4128	2581	24·20
,,	0·51348	108·0	4933	2534	24·65
,,	0·40136	84·48	6165	2475	25·23
,,	0·36366	76·55	6632	2412	25·89
,,	0·34509	72·64	6916	2386	26·17
,,	0·32649	68·72	7231	2362	26·45
,,	0·32279	67·94	7276	2349	26·59
,,	0·31907	67·16	7334	2341	26·68
,,	0·31540	66·39	7353	2320	26·92
160	0·84639	178·1	3214	2721	23·50
,,	0·73602	155·0	3661	2696	23·72
,,	0·62519	131·6	4272	2672	23·93

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
160°	0·51360	108·1	5,105	2623	24·38
"	0·36376	76·57	6,915	2515	25·42
"	0·29061	61·17	8,334	2424	26·38
"	0·27225	57·30	8,780	2391	26·74
"	0·25740	54·18	9,140	2354	27·17
"	0·25370	53·40	9,254	2349	27·22
"	0·25002	52·61	9,344	2338	27·35
"	0·24572	51·72	9,390	2309	27·70
170	0·84662	178·1	3,301	2796	23·39
"	0·66263	155·0	4,158	2757	23·72
"	0·51375	108·1	5,261	2704	24·19
"	0·36386	76·59	7,131	2596	25·20
"	0·25377	53·41	9,704	2462	26·56
"	0·23519	49·50	10,283	2418	27·05
"	0·21659	45·59	10,950	2372	27·58
"	0·20542	43·24	11,388	2339	27·96
"	0·19795	41·67	11,663	2309	28·33
"	0·19425	40·89	11,816	2295	28·49
180	0·84684	178·1	3,381	2864	23·35
"	0·66280	155·0	4,277	2835	23·60
"	0·51388	108·2	5,400	2776	24·10
"	0·40167	84·55	6,780	2723	24·57
"	0·29076	61·20	8,990	2615	25·58
"	0·21664	45·60	11,484	2488	26·89
"	0·17943	37·77	13,183	2366	28·27
"	0·16829	35·42	13,774	2318	28·85
"	0·16091	33·87	14,188	2283	29·29
"	0·15722	33·09	14,446	2271	29·45
"	0·15350	32·31	14,648	2249	29·74
"	0·14975	31·52	14,725	2205	30·33
190	0·84707	178·2	3,486	2954	23·14
"	0·73661	155·0	3,993	2942	23·24
"	0·62569	131·7	4,647	2909	23·50
"	0·43919	92·44	6,498	2854	23·96
"	0·25390	53·44	10,553	2679	25·51
"	0·17948	37·78	13,805	2479	27·58
"	0·16096	33·88	15,006	2416	28·30
"	0·14237	29·97	16,364	2325	29·59
"	0·13498	28·41	16,974	2291	29·83
"	0·13123	27·62	17,279	2268	30·15
"	0·12384	26·07	17,846	2205	31·01
"	0·12017	25·29	18,104	2176	31·42
200	0·84727	178·2	3,559	3016	23·15
"	0·73684	155·0	4,076	3003	23·25
"	0·62584	131·7	4,758	2978	23·46
"	0·43929	92·46	6,628	2911	23·98
"	0·25396	53·46	10,863	2760	25·31
"	0·17952	37·79	14,444	2642	26·94
"	0·16100	33·89	15,701	2527	27·63
"	0·14240	29·97	17,140	2441	28·15
"	0·13501	28·41	17,815	2406	29·03
"	0·12757	26·85	18,494	2359	29·60
"	0·12020	25·29	19,295	2320	30·11
"	0·10507	22·12	20,814	2187	31·94
"	0·10158	21·38	21,336	2167	32·23
"	0·09784	20·59	21,798	2133	32·74
"	0·09418	19·82	22,015	2073	33·68
210	0·84750	178·2	3,628	3075	23·20
"	0·73699	155·1	4,144	3055	23·34
"	0·62601	131·7	4,873	3051	23·38

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
210°	0·43941	92·47	6,791	2984	23·90
”	0·25403	53·47	11,193	2843	25·08
”	0·17957	37·80	14,942	2683	26·58
”	0·16104	33·90	16,324	2629	27·13
”	0·14244	29·98	17,899	2550	27·97
”	0·12390	26·08	19,769	2452	29·12
”	0·10510	22·12	21,992	2312	30·86
”	0·09421	19·82	23,699	2233	31·94
”	0·08664	18·24	24,723	2142	33·30
”	0·08289	17·45	25,458	2111	33·79
”	0·07911	16·65	25,933	2052	34·76
”	0·07533	15·86	26,532	1999	35·68
220	0·88473	186·2	3,515	3111	23·40
”	0·84773	178·4	3,658	3102	23·47
”	0·81051	170·6	3,823	3099	23·49
”	0·73719	155·2	4,173	3077	23·65
”	0·66350	139·7	4,628	3071	23·70
”	0·58901	124·0	5,205	3066	23·74
”	0·51441	108·3	5,916	3043	23·92
”	0·47697	100·4	6,357	3032	24·01
”	0·43953	92·49	6,851	3011	24·17
”	0·40198	84·61	7,468	3002	24·24
”	0·36433	76·68	8,168	2976	24·46
”	0·32709	68·85	9,006	2947	24·70
”	0·29107	61·26	10,030	2920	24·92
”	0·25410	53·48	11,366	2888	25·20
”	0·21687	45·65	13,014	2823	25·78
”	0·17962	37·81	15,214	2733	26·63
”	0·14248	29·99	18,355	2615	27·83
”	0·10513	22·13	22,964	2414	30·15
”	0·06785	14·28	29,632	2011	36·21
”	0·03041	6·40	31,708	964	Liquid visible.
225	0·88481	186·2	3,531	3126	23·52
”	0·84782	178·4	3,684	3123	23·54
”	0·81059	170·6	3,863	3132	23·48
”	0·73726	155·2	4,224	3115	23·61
”	0·66356	139·7	4,681	3107	23·67
”	0·58906	124·0	5,249	3093	23·78
”	0·51446	108·3	5,968	3070	23·95
”	0·47702	100·4	6,402	3058	24·04
”	0·43957	92·52	6,916	3040	24·18
”	0·40213	84·64	7,519	3024	24·31
”	0·36437	76·69	8,251	3007	24·45
”	0·32712	68·85	9,117	2983	24·65
”	0·29110	61·27	10,168	2961	24·84
”	0·27270	57·40	10,755	2933	25·07
”	0·25413	53·49	11,488	2920	25·19
”	0·23552	49·57	12,238	2883	25·51
”	0·21689	45·65	13,160	2855	25·76
”	0·19823	41·72	14,266	2829	26·00
”	0·17963	37·81	15,436	2773	26·51
”	0·16110	33·91	16,921	2727	26·97
”	0·14249	29·99	18,729	2668	27·55
”	0·12395	26·09	20,809	2580	28·51
”	0·10514	22·13	23,365	2457	29·93
”	0·08667	18·24	26,546	2301	31·96
”	0·06785	14·28	30,601	2077	35·42
”	0·06043	12·72	32,389	1957	37·57
”	0·05300	11·16	34,154	1810	40·62
”	0·04929	10·38	34,780	1715	42·89

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
225°	0·03042	6·40	34,792	1058	Liquid visible.
230	0·88493	186·3	3,576	3165	23·47
„	0·84793	178·5	3,722	3157	23·53
„	0·81070	170·6	3,898	3154	23·55
„	0·70065	147·5	4,489	3146	23·62
„	0·58914	124·0	5,308	3127	23·75
„	0·47709	100·4	6,495	3099	23·97
„	0·40207	84·63	7,639	3071	24·18
„	0·32717	68·86	9,257	3029	24·52
„	0·29114	61·28	10,318	3004	24·72
„	0·25416	53·50	11,635	2958	25·06
„	0·21692	45·66	13,367	2900	25·61
„	0·17966	37·81	15,733	2826	26·27
„	0·16112	33·91	17,202	2772	26·80
„	0·14251	29·99	19,082	2720	27·31
„	0·12396	26·09	21,190	2627	28·27
„	0·10515	22·13	23,827	2506	29·64
„	0·08668	18·24	27,144	2353	31·57
„	0·06786	14·28	31,636	2147	34·59
„	0·06044	12·72	33,751	2040	36·41
„	0·05301	11·16	35,650	1890	39·29
„	0·04559	9·595	37,556	1712	43·38
„	0·03042	6·403	38,093	1158	64·10
232	0·88497	186·3	3,604	3190	23·37
„	0·84797	178·5	3,759	3189	23·39
„	0·81074	170·6	3,935	3191	23·37
„	0·66368	139·7	4,772	3167	23·54
„	0·51455	108·3	6,089	3133	23·80
„	0·40209	84·63	7,690	3092	24·12
„	0·29115	61·28	10,377	3022	24·67
„	0·21693	45·66	13,480	2925	25·50
„	0·17967	37·81	15,759	2849	26·17
„	0·14252	29·99	19,108	2724	27·38
„	0·10516	22·13	24,100	2535	29·41
„	0·08668	18·24	27,448	2379	31·34
„	0·06786	14·28	32,091	2178	34·24
„	0·05670	11·93	35,055	1988	37·52
„	0·04930	10·38	37,311	1840	40·53
„	0·04559	9·596	38,071	1736	42·96
„	0·04179	8·849	38,961	1629	45·80
„	0·03042	6·403	39,650	1206	Liquid visible.
234	0·88501	186·3	3,673	3251	23·03
„	0·81077	170·6	3,999	3243	23·14
„	0·66371	139·7	4,862	3227	23·20
„	0·51458	108·3	6,210	3196	23·43
„	0·36445	76·71	8,628	3144	23·80
„	0·25419	53·50	11,969	3042	24·61
„	0·17968	37·81	16,135	2901	25·80
„	0·14253	29·99	19,458	2773	26·99
„	0·10516	22·13	24,504	2577	29·12
„	0·08669	18·24	27,740	2405	31·13
„	0·06787	14·28	32,721	2221	33·71
„	0·05670	11·93	36,030	2043	36·65
„	0·04930	10·38	38,092	1878	39·88
„	0·04559	9·596	39,104	1872	41·99
„	0·04204	8·849	40,048	1683	44·46
„	0·03802	8·002	40,711	1548	48·36
„	0·03042	6·403	40,894	1244	Liquid visible.
236	0·88507	186·3	3,690	3266	23·00

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
236°	0·81083	170·6	4,029	3267	23·00
”	0·66376	139·7	4,891	3246	23·15
”	0·51461	108·3	6,249	3116	23·37
”	0·36448	76·71	8,669	3160	23·78
”	0·25420	53·50	12,073	3069	24·49
”	0·17969	37·81	16,249	2919	25·74
”	0·14254	29·99	19,694	2806	26·78
”	0·10517	22·13	24,872	2616	28·73
”	0·08670	18·24	28,371	2460	30·56
”	0·06787	14·28	33,106	2247	33·45
”	0·05670	11·93	36,477	2068	36·34
”	0·04931	10·38	38,701	1909	39·38
”	0·04560	9·597	39,733	1812	41·49
”	0·04204	8·849	40,705	1712	43·91
”	0·03802	8·002	41,593	1578	47·52
”	0·03042	6·403	42,245	1285	Liquid visible.
237	0·88508	186·3	3,693	3269	23·04
”	0·81083	170·6	4,022	3262	23·09
”	0·66376	139·7	4,892	3247	23·19
”	0·51461	118·3	6,270	3224	23·36
”	0·36448	76·71	8,676	3162	23·81
”	0·25420	53·50	12,094	3075	24·49
”	0·17969	37·81	16,336	2935	25·66
”	0·14254	29·99	19,802	2823	26·68
”	0·10517	22·13	24,980	2627	28·66
”	0·08670	18·24	28,612	2480	30·36
”	0·06787	14·28	33,338	2263	33·28
”	0·05670	11·93	36,634	2077	36·25
”	0·04931	10·38	38,983	1922	39·18
”	0·04560	9·597	39,906	1819	41·39
”	0·04204	8·849	41,123	1729	43·56
”	0·03802	8·002	42,274	1607	46·85
”	0·03042	6·403	43,083	1311	Liquid visible.
238	0·88510	186·3	3,699	3275	23·04
”	0·81085	170·7	4,030	3268	23·08
”	0·66377	139·7	4,896	3250	23·21
”	0·51462	108·3	6,274	3226	23·39
”	0·36449	76·71	8,673	3161	23·87
”	0·25421	53·50	12,087	3073	24·56
”	0·17970	37·81	16,322	2933	25·73
”	0·14254	30·00	19,910	2837	26·59
”	0·10517	22·14	24,988	2628	28·70
”	0·08670	18·25	28,746	2492	30·28
”	0·06787	14·29	33,767	2293	32·92
”	0·05671	11·93	36,854	2090	36·10
”	0·04931	10·38	39,253	1935	38·98
”	0·04560	9·597	40,186	1832	41·10
”	0·04204	8·849	41,412	1741	43·33
”	0·03802	8·002	42,448	1614	46·75
”	0·03422	7·202	43,282	1481	50·94
”	0·03043	6·404	43,694	1329	Liquid visible.
239	0·88514	186·3	3,708	3283	23·03
”	0·81089	170·6	4,029	3268	23·13
”	0·62647	131·9	5,185	3248	23·26
”	0·43973	92·56	7,301	3213	23·54
”	0·25422	53·50	12,161	3091	24·46
”	0·17971	37·81	16,408	2949	25·64
”	0·14254	30·00	19,999	2851	26·52
”	0·10517	22·13	25,262	2657	28·45
”	0·08670	18·24	28,785	2495	30·30

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
239°	0·06788	14·28	33,890	2300	32·86
,,	0·05671	11·93	37,410	2122	35·63
,,	0·04931	10·38	39,504	1948	38·81
,,	0·04560	9·597	40,815	1861	40·62
,,	0·04205	8·849	41,947	1764	42·86
,,	0·03802	8·002	42,954	1633	46·28
,,	0·03422	7·202	43,853	1501	50·38
,,	0·03043	6·404	44,285	1348	56·11
240	0·88516	186·3	3,712	3287	23·04
,,	0·81091	170·7	4,046	3281	23·08
,,	0·62648	131·9	5,198	3257	23·26
,,	0·43975	92·51	7,305	3212	23·58
,,	0·25423	53·50	12,188	3098	24·45
,,	0·17972	37·81	16,500	2979	25·43
,,	0·14255	30·00	19,959	2845	26·62
,,	0·10518	22·13	25,303	2662	28·46
,,	0·08671	18·25	29,037	2518	30·09
,,	0·06788	14·28	33,900	2301	32·92
,,	0·05671	11·93	37,401	2122	35·70
,,	0·04931	10·38	39,865	1966	38·53
,,	0·04560	9·597	41,075	1873	40·44
,,	0·04205	8·850	42,353	1781	42·53
,,	0·03802	8·002	43,585	1657	45·70
,,	0·03422	7·202	44,299	1516	49·97
,,	0·03043	6·404	45,039	1370	55·28
241	0·88518	186·3	3,715	3290	23·07
,,	0·81092	170·7	4,055	3289	23·07
,,	0·62650	131·9	5,212	3260	23·27
,,	0·43976	92·56	7,319	3218	23·58
,,	0·25423	53·50	12,207	3103	24·46
,,	0·17972	37·82	16,535	2971	25·54
,,	0·14255	30·00	20,013	2853	26·50
,,	0·10518	22·13	25,482	2680	28·31
,,	0·08671	18·25	29,277	2538	29·89
,,	0·06788	14·28	34,150	2318	32·74
,,	0·05671	11·93	37,630	2133	35·57
,,	0·04931	10·38	40,087	1977	38·38
,,	0·04560	9·598	41,324	1885	40·27
,,	0·04205	8·850	42,623	1793	42·34
,,	0·03802	8·002	43,866	1668	45·50
242	0·88520	186·3	3,719	3293	23·10
,,	0·81094	170·7	4,062	3294	23·08
,,	0·62651	131·9	5,216	3268	23·27
,,	0·43977	92·56	7,321	3220	23·62
,,	0·25424	53·51	12,238	3111	24·45
,,	0·17973	37·82	16,566	2978	25·54
,,	0·14256	30·00	20,216	2883	26·39
,,	0·10518	22·14	25,554	2688	28·30
,,	0·08671	18·25	29,372	2546	29·86
,,	0·06788	14·29	34,093	2314	32·86
,,	0·05671	11·94	37,769	2142	35·50
,,	0·04932	10·38	40,321	1989	38·24
,,	0·04560	9·598	41,487	1892	40·19
,,	0·04205	8·850	42,658	1724	42·39
,,	0·03802	8·002	44,056	1676	45·39
243·1	0·88522	186·3	3,721	3295	23·12
,,	0·81097	170·7	4,053	3288	23·18
,,	0·66387	139·7	4,951	3287	23·18
,,	0·51470	108·3	6,332	3259	23·08
,,	0·36454	76·71	8,793	3206	23·77

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
243°·1	0·25424	53·51	12,260	3117	24·45
,,	0·17973	37·82	16,611	2985	25·53
,,	0·14256	30·01	20,158	2888	26·39
,,	0·10518	22·14	25,570	2689	28·33
,,	0·08671	18·25	29,438	2552	29·85
,,	0·06788	14·29	34,546	2345	32·50
,,	0·05671	11·94	38,192	2165	35·28
,,	0·04932	10·38	40,753	2015	37·83
,,	0·04560	9·598	41,876	1909	39·91
,,	0 04205	8·850	43,228	1818	41·92
,,	0·03803	8·002	44,367	1687	45·17
244·35	0·88525	186·3	3,751	3322	23·00
,,	0·81100	170·7	4,090	3317	23·02
,,	0·62656	131·9	5,259	3295	23·18
,,	0·43980	92·57	7,387	3249	23·51
,,	0·25426	53·52	12,313	3123	24·46
,,	0·17974	37·83	16,704	3002	25·44
,,	0·14256	30·01	20,269	2889	26·43
,,	0·10519	22·14	25,664	2700	28·30
,,	0·08671	18·25	28,991	2562	29·81
,,	0·06789	14·29	34,657	2353	32·46
,,	0·05672	11·94	38,671	2178	34·92
,,	0·04932	10·38	41,114	2027	37·67
,,	0·04561	9·599	42,394	1934	39·50
,,	0·04205	8·851	43,788	1841	41·48
246°·0	0·88528	186·3	3,750	3321	23·08
,,	0·81102	170·7	4,091	3318	23·09
,,	0·62657	131·9	5,276	3306	23·18
,,	0·43981	92·57	7,465	3284	23·34
,,	0·25426	53·52	12,381	3155	24·29
,,	0·17975	37·83	16,817	3023	25·35
,,	0·14257	30·01	20,430	2913	26·31
,,	0·10519	22·14	25,936	2729	28·09
,,	0·08672	18·25	29,929	2596	29·53
,,	0·06789	14·29	34,928	2371	32·31
,,	0·05672	11·94	38,795	2200	34·82
,,	0·04932	10·38	41,358	2040	37·56
,,	0·04561	9·599	42,658	1945	39·22
,,	0·04205	8·851	44,053	1853	41·36

SERIES III.

34. The amount of alcohol used for the determinations of which the results are given above was too large to admit of values at lower temperatures; a fresh portion was removed, and the weight of the remainder was ascertained by determining the value of P. V. at a temperature at which it became constant at the highest volumes. This temperature was 130°, and the mean value obtained for P. V. was 950·8. From this the weight of alcohol was calculated to be 0·001747 grm.

The following measurements were made :—

T.	Volume.	Sp. vol.	P.	P. V.	Vapour density.
90°	0·84487	483·5	993	839·7	23·47
"	0·77117	441·4	1085	837·3	23·54
"	0·73470	420·5	1135	834·4	23·62
"	0·71638	410·0	1163	833·7	23·65
100	0·84509	483·7	1026	867·7	23·34
"	0·62423	357·3	1385	865·0	23·43
"	0·53019	304·1	1598	849·9	23·83
"	0·51280	293·5	1650	846·7	23·92
110	0·84532	483·8	1062	898·4	23·15
"	0·62440	357·4	1429	892·6	23·30
"	0·43828	250·8	1996	875·2	23·76
"	0·38213	218·7	2259	863·7	24·08
"	0·36330	207·9	2342	851·2	24·43

35. The results of all these determinations of vapour-density are represented, so far as it is possible without introducing confusion, on Plate 4; the ordinates represent pressures, and the abscissæ vapour-densities compared with hydrogen under similar conditions of temperature and pressure; the smaller curve represents the results of the experiments at lower temperatures on a larger scale. The lines are isothermals; and the curve connecting their terminal points gives the densities of the saturated vapour at the corresponding temperatures and pressures. From inspection of this curve it is evident that these results for densities of saturated vapour confirm those obtained by direct measurement at temperatures above 180°; but the previous results are incorrect, below that temperature, for reasons already given. So far as can be judged from these results, the density of the saturated vapour of alcohol decreases with fall of temperature, and corresponding fall of pressure.

36. But from experiments with acetic acid, this is found not to be the case with that substance. On the contrary, the density of its saturated vapour increases rapidly with fall of temperature and pressure. Hence, it appeared necessary to carry out experiments on the density of saturated alcohol-vapour at still lower temperatures, for it was deemed possible that after reaching a minimum density, fall of temperature would produce an increase. The apparatus, which will be fully described in an account of the experiments with ether, consisted of a HOFMANN'S vapour-density apparatus, so modified as to admit of alteration of pressure. The desired temperature was produced by jacketing with running water.

The following results were obtained at 13·0°:—

Volume.	Pressure.	P. V.
ccs.	mms.	
106	15·55	1648
86·7	18·85	1634
77·5	20·85	1616
69·0	23·6	1628
64·0	25·7	1645
62·2	26·35	1639

At a volume of 59 cub. centims. liquid was present.

37. This method involves three readings of heights of mercury, and calculation of a fourth; and as an error of 0·1 mm. makes an alteration in the value of P. V. of 6 to 10 units, the results, although irregular, are well within the limits of experimental error. They show that the product of pressure into volume remained practically constant up to a very small distance from the volume at which condensation began to occur.

38. From measurements at the boiling-point of alcohol under atmospheric pressure, an attempt was made to ascertain the weight of the extremely minute amount of alcohol present.

Volume.	Pressure.	P. V.
ccs.	mms.	
125·9	15·75	1983
123·5	15·85	1958
118·8	16·80	1996
114·9	17·10	1965

From the mean of these results, 1976, the weight of alcohol was calculated to be 0·004166 grm.

Using this weight to calculate the vapour-density at 13°, the number 22·65 was obtained. This result is not unsatisfactory, considering the experimental difficulties; and, in our opinion, it proves that the density of the saturated vapour is practically normal at low temperatures.

39. The densities of the saturated vapour can be deduced from the curves showing the densities of unsaturated vapour; they are represented by the points of intersection of these curves with the horizontal lines which exhibit change of volume of gas in presence of liquid, while pressure remains constant. They were read from the smoothed curve given in Plate 4, and they are as follows:—

T.	Sp. gr.	Sp. vol.	V. D.	T.	Sp. gr.	Sp. vol.	V. D.
°				°			
0	0·000033	30137	23·00	110	0·00486	205·9	24·50
13	0·000073	13655	23·00	120	0·00658	151·9	24·95
20	0·000111	9004	23·00	130	0·00877	114·0	25·43
30	0·000191	5241	23·00	140	0·01152	86·8	25·99
40	0·000315	3170	23·00	150	0·01488	67·2	26·55
50	0·000506	1977	23·10	160	0·01916	52·19	27·40
60	0·00079	1274	23·20	170	0·02446	40·88	28·40
70	0·00119	842·2	23·40	180	0·03115	32·11	29·70
80	0·00174	575·0	23·50	190	0·0397	25·18	31·43
90	0·00250	399·5	23·80	200	0·0508	19·69	33·65
100	0·00351	285·2	24·02	210	0·0655	15·27	36·65

On comparing the results of this table with that previously given in § 22, it will be seen that above 180° the agreement is close, but that, as was expected, the results diverge widely at lower temperatures; above 210° the agreement was perfect.

The values at 0°, and between 13° and 90° are obtained by interpolation on curve 2, Plate 5.

40. *Heats of Vaporisation of Alcohol.*

From these numbers the heats of vaporisation were calculated by the method already mentioned. They are given in the table which follows:—

T. (cent.)	T. (Abs.)	$\frac{t.}{J.}$	$\frac{dp^*}{dt}$	s_1-s_2	L in calories.
0°	273°	0·00642	1·142	30136	220·9
10	283	0·00666	2·061	16113	221·2
20	293	0·00689	3·557	9003	220·6
30	303	0·00713	5·890	5240	220·1
40	313	0·00736	9·378	3169	218·7
50	323	0·00760	14·38	1976	216·0
60	333	0·00783	21·41	1273	213·4
70	343	0·00807	30·93	840·9	209·9
80	353	0·00831	43·30	573·7	206·4
90	363	0·00854	59·29	398·1	201·6
100	373	0·00878	79·09	283·8	197·1
110	383	0·00901	103·26	204·5	190·3
120	393	0·00925	132·33	150·5	184·2
130	403	0·00948	166·48	112·5	177·6
140	413	0·00972	206·32	85·3	171·1
150	423	0·00995	252·08	65·66	164·7
160	433	0·01019	304·17	50·61	156·9
170	443	0·01042	362·67	39·26	148·4
180	453	0·01066	428·9	30·44	139·2
190	463	0·01089	502·65	23·45	128·4
200	473	0·01113	585·7	17·89	116·6
210	483	0·01136	678·85	13·38	103·2

(For temperatures above 210° reference must be made to § 28.)

41. The relations between temperature and heats of vaporisation are graphically represented in the two curves on Plate 5, fig. 1, curve No. 2, represents this relation for vapour-density. The points experimentally determined are indicated by circles. Between 90° and 13° the dotted line shows the probable course of the curve. It is obvious that the error must be extremely small, and it is probable that the vapour-density attains its minimum at a temperature somewhat below 50°.

42. The curve representing latent heats is similarly indicated by circles and dots. That part of it deduced from the interpolated portion of our observations of vapour-density seems to point to a constant value for heat of vaporisation below about 20°, the temperature at which vapour-density becomes normal being about 40°. This would imply that below that temperature the difference between the specific heats of the saturated liquid and saturated vapour is inversely proportional to the absolute temperature; for in the equation $\gamma = c' + \frac{dL}{dt} - \frac{L}{t}$ the expression $\frac{dL}{dt}$ vanishes.

---

* In grams. per square centimetre.

43. As it was difficult to understand the reason of the great divergence between the heats of vaporisation found by Regnault and those calculated from our results we thought it possible that some error in Regnault's determinations of the vapour-pressures of alcohol, which were at first used as the basis of our calculations, might be the cause of this discrepancy. It has already been noticed that the vapour-densities calculated from Regnault's results with heats of vaporisation are impossible; and by taking the vapour-density as normal the calculated curve of heats of vaporisation approaches as near Regnault's as is possible. Now, as the vapour-pressure of alcohol is a datum for the calculation of the value of s_1, and as this value, as also that of $\frac{dp}{dt}$, occurs in the equation

$$L=(s_1-s_2)\times\frac{t}{J}\times\frac{dp}{dt},$$

an error in Regnault's determinations of vapour-pressure, which we have at first employed, would have influenced all the foregoing results, and most markedly those at lower temperatures. We, therefore, thought it advisable to make a fresh series of determinations of the vapour-pressure of alcohol, and used for this purpose the apparatus described in the Trans. Chem. Soc., Jan., 1885. The temperatures are corrected for the change in volume of the bulb of the thermometer by diminution of pressure, which, with the particular thermometer employed, one graduated in 10ths of degrees, by Negretti and Zambra, amounted to an apparent fall of 0·2° on lowering pressure from 763 mms. to 20 mms.

44. The results are as follows :—

T.	P.	T.	P.	T.	P.
°		°		°	
−5	8·60	0·99	13·00	16·69	35·90
−4·67	8·75	1·28	13·15.	17·65	37·90
−4·27	9·20	1·63	13·75	18·55	40·00
−3·36	9·80	2·31	14·20	19·96	43·95
−2·50	10·25	2·78	14·85	20·86	46·55
−1·63	10·75	3·47	15·45	22·55	51·45
−1·60	10·90	4·67	16·90	23·43	53·95
−1·10	11·05	5·43	17·75	24·46	57·60
−0·92	11·35	6·55	18·85	25·37	60·50
−0·79	11·60	7·65	20·15	26·46	64·70
−0·39	11·85	9·15	22·15	27·25	67·60
−0·13	12·05	10·72	24·90	28·03	69·90
+0·09	12·45	12·39	27·60	29·36	75·75
0·54	12·70	14·09	30·60	32·60	90·6
0·70	12·85	15·87	34·00		

45. From these results a curve was constructed, and from it values at definite temperatures were read off. They are compared with those given by Regnault in the 'Mémoires de l'Institut,' vol. xxvi., p. 374.

T.	P. (Reg.)	P. (R. and Y.)
°		
0	12·70	12·24
5	17·62	17·15
10	24·23	23·50
15	32·98	32·10
20	44·46	43·95
25	59·37	59·50
30	78·52	78·05

46. It will be seen from these results that our pressures are uniformly lower than those given by REGNAULT, except at 25°, where there is manifestly a misprint in his figures. The difference in pressure is approximately constant, and is equal to 0·46 mm. The value of $\frac{dp}{dt}$ is considerably changed by this alteration, and the numbers given, except where the contrary is stated, have been derived from the formula, the constants of which were calculated by us for vapour-pressures.

The Critical Point of Alcohol.

47. In the 'Philosophical Transactions' for 1869, p. 583, ANDREWS gives a diagram showing, to some extent, relations between the pressure and volume of carbon dioxide at temperatures near its critical point. From our observations on alcohol we are enabled to give similar diagrams on Plate 6, showing the volumes of 1 gramme. The first of these (fig. 1) comprises observations between 90° and 243·1°. The scale is necessarily a small one. The isothermal for 243·1° has been mapped, and it is to be noticed that all other isothermals between these limits of temperature would fall between that line and the one representing volumes of saturated vapour. The numbers deduced from observations are represented by circles. Fig. 2 shows similar relations at temperatures between 220° and 246° on an enlarged scale, and it also exhibits the compressibility of the liquid. The highest temperature at which it was possible to measure both liquid and gas was 242·25°; above that temperature measurement of gas was uncertain, owing to the slow rate at which condensation or evaporation proceeded. A successful measurement of the volume of the liquid was made at 242·6°, but it was still possible to distinguish liquid from gas at 243·0°; at 243·1° the meniscus appeared to broaden and became indistinct. It disappeared absolutely on the least decrease of volume, owing to heat developed by compression, and it reappeared on increasing volume. The apparent critical point was therefore at this temperature, but the pressure remained perfectly constant during considerable change of volume. A similar phenomenon has been noticed by ANSDELL, and we agree with him that the real critical point must lie somewhat higher. In the diagram on Plate 6 a dotted line has been drawn connecting the curves showing the volumes of

saturated vapour and of liquid. The summit of this surface, which represents volumes of gas in contact with liquid, if correctly drawn, would give the relation between temperature, pressure, and volume at the critical point. It appears to us impossible to obtain direct measurements of this portion of the curve. There must, therefore, necessarily be some uncertainty as regards all three.

On Plate 7 the relations between the weight of one cubic centimetre of saturated vapour and liquid are shown. Curve No. 1 exhibits this relation between 40° and 242·5°; and curve No. 2 between 225° and 242·5° on an enlarged scale.

It is evident, however, from these results that the critical temperature must lie within 0·5 of a degree above or below 243·6°, that the critical pressure must be nearly 47,700 mms., and that the critical volume cannot be far from 3·5, *i.e.*, one gramme of alcohol at the critical point must occupy about 3·5 ccs.; otherwise expressed, the specific gravity at the critical point is nearly 0·28.

NOTE.

After this memoir had been read (May, 1885), an account of experiments by AMAGAT (Compt. Rend., xcix., p. 1153) on the compressibility of air was noticed. AMAGAT'S reputation and the method he adopted are a sufficient guarantee for their accuracy; and, although these results differ considerably from REGNAULT'S, which, moreover, had reference only to pressures below 20,000 mms., and were therefore not available for our purpose, we have felt justified in making use of them. This has necessitated a recalculation of all the pressures, values of *p.v.*, and vapour-densities given in this paper, and has led us to modify some of the conclusions in the memoir as read in 1885. It was also thought advisable to use BIOT'S formula, and to substitute numbers for pressure calculated by its help, instead of by the method of differences which was at first employed. The use of this formula enabled us to obtain more accurate values for $\frac{dp}{dt}$ than was possible by any graphical means, and, as a result of these alterations, the curve representing heats of vaporisation is much more regular than we at first supposed; besides, it passes between the points obtained from direct measurement by ANDREWS, and by FAVRE and SILBERMANN. The diagrams have also been reconstructed so as to represent accurately the corrected numbers.

IV. *On the Theory of Lubrication and its Application to Mr.* BEAUCHAMP TOWER'S *Experiments, including an Experimental Determination of the Viscosity of Olive Oil.*

By Professor OSBORNE REYNOLDS, *LL.D., F.R.S.*

Received December 29, 1885,—Read February 11, 1886.

[PLATE 8.]

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SECTION I.—INTRODUCTORY.

1. LUBRICATION, or the action of oils and other viscous fluids to diminish friction and wear between solid surfaces, does not appear to have hitherto formed a subject for theoretical treatment. Such treatment may have been prevented by the obscurity of the physical actions involved, which belong to a class as yet but little known, namely, the boundary or surface actions of fluids; but the absence of such treatment has also been owing to the want of any general laws discovered by experiment.

The subject is of such fundamental importance in practical mechanics, and the opportunities for observation are so frequent, that it may well be a matter of surprise that any general laws should have for so long escaped detection.

Besides the general experience obtained, the friction of lubricated surfaces has been the subject of much experimental investigation by able and careful experimenters. But, although in many cases empirical laws have been propounded, these fail for the most part to agree with each other and with the more general experience.

2. The most recent investigation is that of Mr. BEAUCHAMP TOWER, undertaken at the instance of the Institution of Mechanical Engineers. Mr. TOWER's first report was published November, 1883, and his second report in 1884 ("Proc. Inst. Mechanical Engineers").

In these reports Mr. TOWER, making no attempt to formulate, states the results of experiments apparently conducted with extreme care and under very various and well-chosen circumstances. Those results which were obtained under the ordinary conditions of lubrication so far agree with the results of previous investigators as to show a want of any regularity. But one of the causes of this want of regularity, irregularity in the supply of the lubricant, appears to have occurred to Mr. TOWER early in his investigation, and led him to include amongst his experiments the unusual circumstances of surfaces completely immersed in oil. This was very fortunate, for not only do the results so obtained show a great degree of regularity, but while making these experiments he was accidentally led to observe a phenomenon which, taken with the results of his experiments, amounts to a crucial proof that in these experiments with the oil bath the surfaces were completely and continuously separated by a film of oil; this film being maintained by the motion of the journal, although the pressure in the oil at the crown of the bearing was shown by actual measurement to be as much as 625 lbs. per sq. inch above the pressure in the oil bath.

These results obtained with the oil bath are very important, notwithstanding that the condition is not common in practice. They show that with perfect lubrication a definite law of variation of the friction with the pressure and velocity holds for a particular journal and brass. This strongly implies that the irregularity previously found was due to imperfect lubrication. Mr. TOWER has brought this out:—Substituting for the bath an oily pad, pressed against the free part of the journal, and making it so slightly greasy that it was barely perceptible to the touch, he again found considerable regularity in the results; these, however, were very different from those with the bath. Then with intermediate lubrication he obtained intermediate results, of which he says:—"Indeed, the results, generally speaking, were so uncertain and irregular that they may be summed up in a few words. The friction depends on the quantity and uniform distribution of the oil, and may be anything between the oil bath results and seizing, according to the perfection or imperfection of the lubrication."

3. On reading Mr. TOWER's report it occurred to the author as possible that in the case of the oil bath the film of oil might be sufficiently thick for the unknown boundary actions to disappear, in which case the results would be deducible from the equations of hydrodynamics. Mr. TOWER appears to have considered this, for he remarks that according to the theory of fluid friction the resistance would be as the square of the velocity, whereas in his results it does not increase according to this law. Considering how very general the law of resistance as the square of the velocity is with fluids, there is nothing remarkable in the assumption of its holding in such a case. But the study of the behaviour of fluid in very small channels, and particularly the recent determination by the author of the critical velocity at which this law changes from that of the square of the velocity to that of the simple ratio, shows that with such highly viscous fluids as oils, such small spaces as those existing between the journal and its bearing, and such limited velocity as that of the surface of the journal, the resistance would vary, *cœteris paribus*, as the velocity. Further, the thickness of the oil film would not be uniform and might be affected by the velocity, and as the resistance would vary, *cœteris paribus*, inversely as the thickness of the film, the velocity might exert in this way a secondary effect on the resistance; and, further still, the resistance would depend on the viscosity of the oil, and this depends on the temperature. But as Mr. TOWER had been careful to make all his experiments in the same series with the journal at a temperature of 90° Fahr., it did not at first appear that there could be any considerable temperature effect in his results.

4. The application of the hydrodynamical equations to circumstances similar in so far as they were known to those of Mr. TOWER's experiments, at once led to an equation between the variation of pressure over the surface and the velocity, which equation appeared to explain the existence of the film of oil at high pressure. This equation was mentioned in a paper read before Section A. of the British Association at Montreal, 1884. It also appears from a paragraph in the President's Address (Brit. Assoc. Rep., 1884, p. 14) that Professor STOKES and Lord RAYLEIGH had simultaneously arrived at a similar result. At that time the author had no idea of attempting its integration. On subsequent consideration, however, it appeared that the equation might be transformed so as to be approximately integrated, and the theoretical results thus definitely compared with the experimental.

5. The result of this comparison was to show that with a particular journal and

brass the mean thickness of the film of oil would be sensibly constant, and hence, if the viscosity was constant, the resistance would increase directly as the speed. As this was not in accordance with Mr. TOWER's experiments, in which the resistance increased at a much slower rate, it appeared that either the boundary actions became sensible or that there must have been a rise in the temperature of the oil which had escaped the thermometers used to measure the temperature of the journal.

That there would be some excess of temperature in the oil film on which all the work of overcoming the friction is spent is certain; and after carefully considering the means of escape of this heat, it seems probable that there would be a difference of several degrees between the oil bath and the film of oil.

This increase of temperature would be attended by a diminution of viscosity, so that as the resistance and temperature increased with the velocity the viscosity would diminish and cause a departure from the simple ratio.

6. In order to obtain a quantitative estimate of these secondary effects, it was necessary to know exactly the relation between the viscosity and temperature of the lubricant used. For this purpose an experimental determination was made of the viscosity of olive oil at different temperatures as compared with the known viscosity of water. From the results of these experiments an empirical formula has been deduced, by means of which definite expressions have been obtained for the approximate variation of the viscosity with the speed and load. Taking these variations of viscosity into account, the results obtained from the hydrodynamical theory are brought into complete accordance with these experiments of Mr. TOWER. Thus we have not only an explanation of the very novel phenomena brought to light by these experiments, and what appears to be an important verification of the assumptions on which the theory of hydrodynamics is founded, but we also find, what is not shown in the experiments, how the various circumstances under which the experiments have been made affect the results.

7. Two circumstances particularly are brought out in the theory as principal circumstances which seem to have hitherto entirely escaped notice, even that of Mr. TOWER.

One of these is the difference in the radii of the journal and of the brass or bearing.

It is well known that the fitting between the journal and its bearing produces a great effect on the carrying power of the journal, but this fitting is rather supposed to be a matter of smoothness of surface than a degree of correspondence in radii. The radius of the bearing must always be as much larger than that of the journal as is necessary to secure an easy fit; but more than this, I think, has never been suggested.

Now it appears from the theory that if viscosity were constant the friction would be inversely proportional to the difference in radii of the journal and the bearing, and this although the arc of contact is less than the semicircumference. Taking the temperature into account, it appears from the comparison of the theoretical results with the experimental that at a temperature of 70·5° Fahr. the radius of one of the brasses used was ·00077 inch greater than that of the journal, while at a temperature of 70° Fahr. that of the other was ·00084 inch, or 9 per cent. larger than the first.

These two brasses were probably both bedded to the journal in the same way, and had neither of them been subjected to any great amount of wear, so that there is nothing surprising in their being so nearly the same fit. It would be extremely interesting to find whether prolonged wear of the brass tends to preserve or destroy the fit. This does not appear from Mr. TOWER's experiments. It does appear, however, that the brass expands with an increase of temperature more than the journal, and that its radius increases as the load increases in a very definite manner.

Another circumstance brought out by the theory, and remarked on both by Lord RAYLEIGH and the author at Montreal, but not before expected, is that the point of nearest approach of the journal to the brass is not by any means in the line of the load, and, what is still more contrary to common supposition, is on the *off*[*] side of the line of load.

This circumstance, the reason for which is rendered perfectly clear by the conditions of equilibrium, at once accounts for a singular phenomena mentioned by Mr. TOWER, viz., that the journal having been run in one direction until the initial tendency to heat had entirely disappeared, on being reversed it immediately began to heat again; but this effect stopped when the process had been often repeated. The fact being that running in one direction the brass had been worn to the journal only on the *off* side for that direction, so that when the motion was reversed the new *off* side was like a new brass.

7A. The circumstances which determine the greatest load which a bearing will carry with complete lubrication, *i.e.*, with the film of oil extending between brass and journal throughout the entire arc, are definitely shown in the theory.

The effect of increasing the load beyond a certain small value being to cause the brass to approach nearer to the journal at a point H which moves from A towards O as the load increases, and when the load is such that the least separating distance ca is about half the difference of radii a, the angular position of H is 40° to the off side of O, the middle of the brass. At this point the pressure in the oil film is everywhere greater than at A and B, the extremities of the brass, but when the load further increases the pressure towards A on the off side becomes smaller or negative. This when sufficient

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[*] "On" and "off" sides of the line of load are used by Mr. TOWER to express respectively the sides of approach and succession, as B and A in the figure, the arrow indicating the direction of rotation.

will cause rupture in the oil film, which will then only bextend etween the brass and journal over a portion of the whole arc and a smaller portion as the load increases. Thus, since the amount of negative pressure which the oil will bear depends on circumstances which are uncertain, the limit of the safe load for complete lubrication is that which causes the least separating distance to be half the difference of radii of the brass and journal.

The rupture of the oil film does not take place at the point of nearest approach, and hence the brass may still be entirely separate from the journal, and could the integrations be effected it would be possible to deal as definitely with this condition as with that of complete lubrication; but these difficulties have limited the actual application of the theory to complete lubrication. This however by no means requires an oil bath, but merely sufficient oil on the journal.

What happens when the supply of oil is limited, *i.e.*, insufficient for complete lubrication, cannot be definitely expressed without further integrations; but sufficient may be seen to show that the brass will still be completely separated from the journal, although the separating film will not touch the brass, except over a limited area; but in this case it is easy to show by general reasoning that in the one extreme, where the supply of oil is limited, the friction increases directly as the load and is independent of the velocity, while in the other, where the oil is abundant, the circumstances are those of the oil bath.

The effect of the limited length of the journal is also apparent in the equations, as is also the effect of necking the shaft to form the journal, so that the ends of the brass are against flanges on the shaft.

The theory is perfectly applicable to cases in which the direction of the load on the bearing varies, as with the crank pin and with the bearings of the crank shaft of the steam-engine; but these cases have not been considered, as there are no definite experiments to compare.

8. Although in the main the present investigation has been directed to the circumstances of Mr. TOWER's experiments, viz., a cylindrical journal revolving in a cylindrical brass, it has, on the one hand, been found necessary to proceed from the general equations of equilibrium of viscous fluids, and, on the other hand, to consider somewhat generally the physical property of viscosity and its dependence on temperature.

The property of viscosity has been discussed at length in Section II.; which section also contains the account of an experimental investigation as to the viscosity of olive oil.

The general theory deduced from the hydrodynamical equations for viscous fluids, with the methods of application, is given in Sections IV., V., VI., VII., and VIII.

As there are some considerations which cannot be taken into account in the more general method, which method also tends to render obscure the more immediate purpose of the investigation, a preliminary discussion of the problem, illustrated by aid of the graphic method, has been introduced as Section III. Finally, the definite application of the theory to Mr. Tower's experiments is given in Section IX.

Section II.—The Properties of Lubricants.

9. *The Definition of Viscosity.*

In distinguishing between solid and fluid matter, it is customary to define fluid as a state of matter incapable of sustaining tangential or shearing stress. This definition, however, as is well known, is only true as applied to *actual* fluids when at rest. The resistance encountered by water and all known fluids flowing steadily along parallel channels, affords definite proof that in certain states of motion all actual fluids will sustain shearing stress. These actual fluids are, therefore, called in the language of mathematics imperfect or viscous fluids.

In order to obtain the equations of motion of such fluids, it has been necessary to define clearly the property of viscosity. This definition has been obtained from the consideration that to cause shearing stress in a body it is necessary to submit it to forces tending to change its shape. Forces tending to cause a general motion, whether linear, revolving, uniform expansion, or uniform contraction, call forth no shearing stress.

Using the term *distortion* to express change of shape, apart from change of position, uniform expansion, or contraction, the viscosity of a fluid is defined as the shearing stress caused in the fluid while undergoing distortion, and the shearing stress divided by the rate of distortion is called the coefficient of viscosity, or, commonly, the viscosity of the fluid.

This is best expressed by considering a mass of fluid bounded by two parallel planes at a distance a, and supposing the fluid between these planes to be in motion in a direction parallel to these surfaces with a velocity which varies uniformly from 0 at one of these surfaces to u at the other. Then the rate of distortion is

$$\frac{u}{a}$$

and the shearing stress on a plane parallel to the motion is expressed by

$$f=\mu\frac{u}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

μ being the coefficient of viscosity or the modulus of the resistance to distortional motion.

10. *The Character of Viscosity.*

In dealing with ideal fluids, it is of course allowable to consider μ as being zero or having any conceivable value; but practically, as regards natural philosophy, the value of any such considerations depends on whether the calculated behaviour of the ideal fluid is found to agree with the behaviour of the actual fluids—whether taking a particular fluid, a value of μ can be found such that the values of f calculated by equation (1) agree with the values of f determined by experiments for all values of a and u.

In the mathematical theory of viscous fluid, μ is assumed to be constant for a particular fluid. This supposition is sometimes justified by reference to some assumed dynamical constitution of fluids; but apart from such hypotheses there is no more ground for supposing a constant value for μ than there is for supposing a particular law of gravitation, in other words, there is no ground at all. If a particular value of μ is found to bring the calculated results into agreement with all experimental results, then this value of μ defines a property of actual fluids, and of course it has been with this object that the mathematical theory of μ has been studied.

The chief question as regards μ is a simple one—within a particular fluid is μ constant? In other words, is viscosity a property of a fluid like inertia which is independent of its motion? If it is, our equations may be useful; if it is not then the introduction of μ into the equations renders them so complex that it is almost hopeless to expect anything from them.

Another question of scarcely less practical importance relates to the character of μ near the bounding surfaces of the fluid. If μ is constant in the fluid, does it change its value near the boundary of the fluid? Is there anything like slipping between the fluid and a solid boundary with which it is in contact?

As regards the answers to these questions the present position is somewhat as follows:—

11. *The Two Viscosities.*

The general experience that the resistance varies as the square of the velocity is an absolute proof that μ is not constant unless a restricted meaning be given to the definition of viscosity, excluding such part of the resistance as may be due, in the way explained by Prof. STOKES,[*] to internal eddies or cross streams, however insensible these may be, so long as they are not simply molecular motions.

On the other hand in the definite experiments made by COLOMB, and particularly by POISEUILLE, it was found that the resistance was proportional to the velocity, and therefore that μ was absolutely constant—*i.e.*, independent of the velocity.[†]

To meet this discordance it has been supposed that μ varied with the rate of distortion—*i.e.*, is a function of u/a, but is sensibly constant when u/a is small.[‡]

To assume this, however, is to neglect POISEUILLE'S experiments, in which he found for water the resistance absolutely proportional to the velocity in a tube ·6 mm.

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[*] STOKES'S Reprint, vol. i., p. 99.

[†] Paris Mém. Savans Étrang., tom. 9 (1846), p. 434.

[‡] LAMB'S "Motion of Fluids," 1879, Art. 180.

diameter up to a velocity of 6 metres per second, which corresponds to a value of $u/a=20,000$.

On the other hand it is found by DARCY[*] and others in large tubes that the resistance varies as the square of the velocity for values of $\frac{u}{a}$, as low as 1. Thus in a tube of ·6 mm. we have μ constant for all rates of distortion below 20,000, while in a tube of 500 mm. diameter μ is a function of the distortion for all values greater than 1.

It is, therefore, clear that if μ is a function of the distortion it must also be a function of the dimensions of the channels, and in that case μ cannot be considered as a property of the fluid only.

The change in the law of resistance from the simple ratio has, however, been shown by the author to be due to a change in the character of the motion of the fluid from that of direct parallel motion to that of sinuous or eddying motion.[†]

In the latter case, although the mean motion at any point taken over a sufficient time is parallel to the pipe, it is made up of a succession of motions crossing the pipe in different directions.

The question as to whether, in the case of sinuous motion, μ is to be considered as a function of the velocity or not, depends on whether we regard f as expressing the instantaneous shearing stress at a point, or the mean over a sufficient time. Whether we regard the symbols in the equations of motion as expressing the instantaneous motion or the mean taken over a sufficient time.

If the latter, then μ must be held to include, in addition to the mean stress, the momentum per second parallel to u carried by the cross streams in the negative direction across the surface over which f is measured.

If, however, we regard the motion at each instant, then we must restrict our definition of viscosity by making f the instantaneous value of the intensity of resistance at a point.

This is a quantity which we have, and can have no means of measuring except under circumstances which secure that f is constant for all points over a given surface, and for all instants over a given time.

It thus appears that there are two essentially distinct viscosities in fluids. The one a mechanical viscosity arising from the molar motion of the fluid, the other a physical property of the fluid. It is worth while to point out that, although the conditions under which the first of these, the mechanical viscosity, can exist depend primarily on the physical viscosity, the actual magnitudes of these viscosities are independent, or are only connected in a secondary manner. This is shown by a very striking but little noticed fact. When the motion of the fluid is such that the resistance is as the square of the velocity, the magnitude of this resistance is sensibly quite independent of the character of the fluid in all respects except that of density. Thus, when in a particular pipe the velocity of oil or treacle is sufficient for the resistance to vary as the square of the velocity, the resistance is practically the same as it would be with water at the same velocity, while the physical viscosity of water is more than one hundred times less.

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[*] Recherches Expl. Paris, 1852.

[†] "An Experimental Investigation of the circumstances which determine whether the Motion of Water shall be Direct or Sinuous." Phil. Trans., vol. 174 (1883), p. 935.

The answer, then, to the question as to the constancy of μ may be clearly given—μ measures a physical property of the fluid which is independent of its motion. But in this sense μ is the coefficient of instantaneous resistance to distortion at a point moving with the fluid.

This restriction is equivalent to restricting the applications of the equations of motion for a viscous fluid to the cases in which there are no eddies or sinuosities.

This, as shown by the author, is the case in parallel channels so long as the product of the velocity, the width of the channel, and the density of the fluid divided by μ is less than a certain constant value. In a round tube this constant is 1400, or

$$\frac{\mathrm{D}v\rho}{\mu} < 1400.$$

At a temperature of 50°, we have with a foot, as unit of length, for water:—

$$\frac{\mu}{\rho} = 0{\cdot}00001428$$

$$\mathrm{D}v < {\cdot}02,$$

so that if D, the diameter of the channel, be ·001 inch, v would have to be at least 240 feet per second for the resistance to vary other than as the velocity.

As regards the slipping at the boundaries, POISEUILLE'S experiments, as well as those of the author, failed to show a trace of this, although f reached the value of 0·702 lb. per square inch, so that within this limit it may be taken as proved that there is no slipping between any solid surface and water. With other fluids, such as mercury in glass tubes, it is possible that the case may be different; but, as regards oils, the probability seems to be that the limit within which there is no slipping will be much higher than with water.

12. *Experimental determination of the value of μ for olive oil.*

Since the value of μ for water is known for all moderate temperatures, in order to obtain the value for oil it is only necessary to ascertain the relative times taken by the same volumes of oil and water to flow through the same channel, care being taken to make the channel such that there are no eddies and that the energy of motion is small compared with the loss of head.

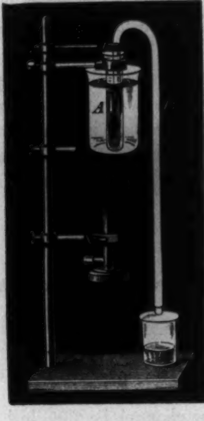
These times are proportional to

$$\frac{\mu}{p}.$$

Where p is the fall of pressure; therefore the times multiplied by the respective falls of pressure are proportional to the viscosities.

The arrangement of apparatus used is shown in fig. 2.

Fig. 2.



The test tube (A) containing the fluid to be tested was fixed in a beaker of water, which was heated and maintained at any required temperature from below.

A syphon (B), made of glass tube $\frac{3}{16}$ inch internal diameter, with the extremity of its short limb drawn down to capillary size for a length of about 6 inches, this six inches being bent up and down so as only to occupy some 2 inches at the bottom of the test tube. The long limb of the syphon extended to about 2 feet below the mean level of the fluid in the test tube. Two marks on the test tube at different levels served to show when a definite volume had been withdrawn.

The syphon used was the same for each set of experiments on oil and water, so that the pressure urging the fluid through the tube was proportioned to the density of the fluids—that is, it was 1·915 as great for oil as water, disregarding the effect of the variation of temperature on volume, which in no case amounted to 1 per cent.

Experiments were first made with water at different temperatures, the times taken for the water to fall from the first mark to the second being carefully noted. The syphon was then dried and replaced and oil substituted for water.

Two sets of similar but entirely different apparatus were used on different occasions, different samples of oil being used. In the first set the experiments on oil were made at temperatures from 95° to 200° Fahr.; in the second set, from 61° to 120° Fahr. In so far as the temperatures overlapped, the viscosities for the two oils agreed to within 4 per cent., but as the law of variation of the viscosity seemed to change rapidly at about 140° Fahr., only the second set have been recorded. These are shown in Table I.

From POISEUILLE'S experiments it is found that, measuring viscosity in pounds on the square inch, for water at a temperature of 61° Fahr.,

$$\mu = 10^{-7} \times 1{\cdot}61.$$

Adopting this value of μ for the experiments on water at 61° Fahr., the other experimental values of μ for water at different temperatures, obtained as being in the ratios of the times, were found to be in very close agreement with those calculated from POISEUILLE'S law for the respective temperatures. This tested the efficiency of the apparatus. It has not been thought necessary to record any experiment on water except at the temperature of 61° Fahr.

The experimental value of μ for oil are in the ratios of the times multiplied by ·915, the specific gravity of oil; these are given as the experimental values of μ in the table. Another column contains the values of μ for oil, calculated from an empirical formula fitted to the experimental values.

This formula was found by comparing the logarithms of the experimental values of μ. It appeared that the differences in these logarithms were nearly proportional to the differences in the corresponding temperatures, or that T being temperature in degrees Fahr.,

$$\log \mu_1 - \log \mu_2 = {\cdot}0096(\mathrm{T}_2 - \mathrm{T}_1)$$

in degrees Centigrade

$$\log \mu_1 - \log \mu_2 = {\cdot}00535(\mathrm{T}_2 - \mathrm{T}_1)$$

whence since

$${\cdot}0096 = {\cdot}0221 \log_{10} e$$
$${\cdot}00535 = {\cdot}0123 \log_{10} e$$

for degrees Fahrenheit

$$\frac{\mu_1}{\mu_2} = e^{-{\cdot}0221(\mathrm{T}_1 - \mathrm{T}_2)}$$

for degrees Centigrade . . . . (2)

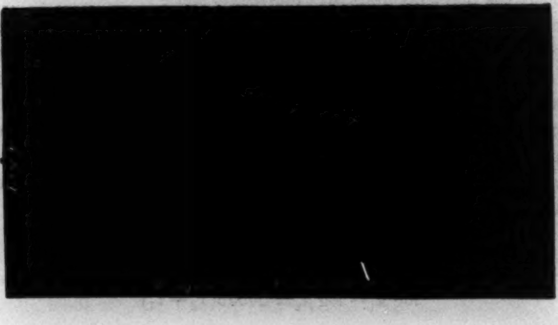
$$\frac{\mu_1}{\mu_2} = e^{-{\cdot}0123(\mathrm{T}_1 - \mathrm{T}_2)}$$

This ratio holds well within the experimental accuracy from temperatures ranging from 61° to 120° Fahr. This is shown in the table, and again in fig. 3, in which the ordinates are proportional to $\log \mu$, the abscissæ being proportional to the corresponding temperatures.

TABLE I.—Viscosity of Oil compared with Water: 11 April, 1884.

Number.	Third.	Temperature.		Time seconds.	$\frac{\mu}{10^7}$ experimental.	log μ experimental.	log μ calculated.	$\frac{\mu}{10^7}$ calculated.
		Fahrenheit.	Centigrade.					
1	Water. .	60°	15·5°	25	1·640			
2	" . .	"	"	"	"			
3	" . .	"	"	"	"			
4	Olive oil .	61	16	2040	123·00	$\bar{5}$·08990	$\bar{5}$·090133	123·06
5	" .	81		1350	81·00	6·90848	$\bar{6}$·89807	79·08
6	" .	94		1000	60·00	$\bar{6}$·77815	6·78290	59·34
7	" .	120		555	33·40	6·52375	$\bar{6}$·52375	33·40

Fig. 3.



13. *The Comparative Values of μ for Different Fluids and Different Systems of Units.*

The values of μ given by different writers for air and water, are expressed in various units of force and length, so that it is a matter of some trouble to compare them. To facilitate this for the future comparative values are here given. Those for water have been deduced from POISEUILLE's formula, for air from MAXWELL's formulæ, and for olive oil from the experiments recorded in the previous article.

The units of length, mass, and time, being respectively the centimetre, gramme, and second, in which case the unit of force is the weight of one 980·5th (g) part of a gramme, expressing temperature in degrees Centigrade by T and putting

$$P^{-1}=1+0{\cdot}0336793T+0{\cdot}0002209936T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for

$$\left.\begin{array}{lll} \text{water} & . \ . & \mu=0\cdot0177931\mathrm{P} \\ \text{air} & . \ . \ . & \mu=0\cdot0001879(1+0\cdot00366\mathrm{T}) \\ \text{olive oil} & . \ . & \mu=3\cdot2653\, e^{-\cdot0123\mathrm{T}}\text{*} \end{array}\right\} \quad . \ . \ . \ . \ . \ . \quad (4)$$

With the same unit of length, but g grammes as unit of mass and 1 gramme as unit of force, the values of μ are for

$$\left.\begin{array}{lll} \text{water} & . \ . \ . & \mu=0\cdot000019792\mathrm{P} \\ \text{air} & . \ . \ . \ . & \mu=0\cdot00000019153(1+\cdot00366\mathrm{T}) \\ \text{olive oil} & . \ . & \mu=0\cdot0033303\, e^{-\cdot0123\mathrm{T}} \end{array}\right\} \quad . \ . \ . \ . \ . \quad (5)$$

The units of length and mass being the foot and pound and the temperature in degrees Fahr. for

$$\left.\begin{array}{lll} \text{water} & . \ . \ . & \mu=0\cdot0011971\mathrm{P} \\ \text{air} & . \ . \ . \ . & \mu=0\cdot000011788(1+\cdot0020274\mathrm{T}) \\ \text{olive oil} & . \ . & \mu=0\cdot21943\, e^{-\cdot0221\mathrm{T}} \end{array}\right\} \quad . \ . \ . \ . \quad (6)$$

With the same unit of length the unit of mass being $g(32\cdot1695)$ lbs. and the unit of force 1 lb. for

$$\left.\begin{array}{lll} \text{water} & . \ . \ . & \mu=0\cdot000037166\mathrm{P} \\ \text{air} & . \ . \ . \ . & \mu=0\cdot00000036645(1+\cdot0020274\mathrm{T}) \\ \text{olive oil} & . \ . & \mu=0\cdot0068213\, e^{-\cdot0221\mathrm{T}} \end{array}\right\} \quad . \ . \ . \ . \quad (7)$$

Taking the unit of length 1 inch and the unit of force 1 lb. for

$$\left.\begin{array}{lll} \text{water} & . \ . \ . & \mu=0\cdot000000258105\mathrm{P} \\ \text{air} & . \ . \ . \ . & \mu=0\cdot0000000025447(1+\cdot0020274\mathrm{T}) \\ \text{olive oil} & . \ . & \mu=0\cdot00004737\, e^{-\cdot0221\mathrm{T}} \end{array}\right\} \quad . \ . \ . \ . \ . \quad (8)$$

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* For olive oil the values of μ have only been tested between the limits of temperature 16° and 49° C. or 61° and 120° Fahr.

SECTION III.—GENERAL VIEW OF THE ACTION OF LUBRICATION.

14. *The case of two nearly parallel Surfaces separated by a viscous Fluid.*

Let AB and CD (fig. 4) be perpendicular sections of the surfaces, CD being of limited but great extent compared with the distance h between the surfaces, both surfaces being of unlimited length in a direction perpendicular to the paper.

Fig. 4.

Case 1. *Parallel Surfaces in Relative Tangential Motion.*—In fig. 5 the surface CD is supposed fixed, while AB moves to the left with a velocity U.

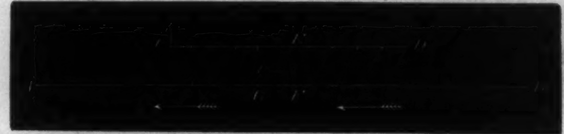
Then by the definition of viscosity (Art. 9) there will be a tangential resistance

$$F=\mu\frac{U}{h},$$

and the tangential motion of the fluid will vary uniformly from U at AB to zero at CD. Thus if FG (fig. 5) be taken to represent U, then PN will represent the velocity in the fluid at P.

The slope of the line EG therefore may be taken to represent the force F, and the direction of the tangential force on either surface is the same as if EG were in tension. The sloping lines therefore represent the condition of motion and stress throughout the film (fig. 5).

Fig. 5.



Case 2. *Parallel Surfaces approaching with no Tangential Motion.*—The fluid has to be squeezed out between the surfaces, and since there is no motion at the surface, the horizontal velocity outward will be greatest half-way between the surfaces, nothing at O the middle of CD, and greatest at the ends.

If in a certain state of the motion (shown by dotted line, fig. 6) the space between AB and CD be divided into 10 equal parts by vertical lines (fig. 6, dotted figure), and these lines supposed to move with the fluid, they will shortly after assume the positions of the curved lines (fig. 6), in which the areas included between each pair of curved lines is the same as in the dotted figure. In this case, as in Case 1, the distance QP will represent the motion at any point P, and the slope of the lines will represent the tangential forces in the fluid as if the lines were stretched elastic strings. It is at once seen from this that the fluid will be pulled towards the middle of CD by the viscosity as though by the stretched elastic lines, and hence that the pressure will be greatest at O and fall off towards the ends C and D, and would be approximately represented by the curve at the top of the figure.

Fig. 6.

Case 3. *Parallel Surfaces approaching with Tangential Motion.*—The lines representing the motions in Cases 1 and 2 may be superimposed by adding the distances PQ in fig. 6 to the distances PN in fig. 5.

The result will be as shown in fig. 7, in which the lines represent in the same way as before the motions and stresses in the fluid where the surfaces are approaching with tangential motion.

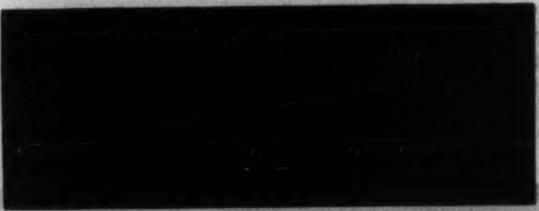
Fig. 7.

In this case the distribution of pressure over CD is nearly the same as in Case 2, and the mean tangential force will be the same as in Case 1. The distribution of the friction over CD will, however, be different. This is shown by the inclination of the curves at the points where they meet the surface. Thus on CD the slope is greater on the left and less on the right, which shows that the friction will be greater on the left and less on the right than in Case 1. On AB the slope is greater on the right and less on the left, as is also the friction.

Case 4. *Surfaces inclined with Tangential Movement only.*—AB is in motion as in Case 1, and CD is inclined as in fig. 8.

The effect in this case will be nearly the same as in the compound movement (Case 3).

Fig. 8.



For if corresponding to the uniform movement U of AB, the velocity of the fluid varied uniformly from the surface AB to CD, then the quantity carried across any section PQ would be

$$PQ \times \frac{U}{2},$$

and consequently would be proportional to PQ; but the quantities carried across all sections must be the same, as the surfaces do not change their relative distances; therefore there must be a general outflow from any vertical sections PQ, P′Q′ given by

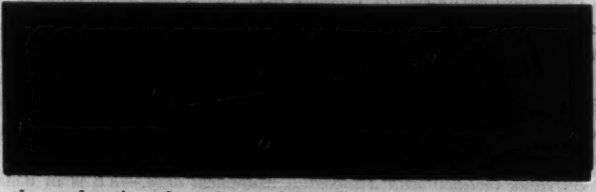
$$\frac{U}{2}(PQ - P'Q').$$

This outflow will take place to the right and left of the section of greatest pressure. Let this be P_1Q_1, then the flow past any other section PQ

$$\frac{U}{2}(PQ - P_1Q_1)$$

to the right or left according as PQ is to the right or left of P_1Q_1. Hence at this section the motion will be one of uniform variation, and to the right and left the lines showing the motion and friction will be nearly as in fig. 7. This is shown in fig. 9.

Fig. 9.



This is the explanation of continuous lubrication.

The pressure of the intervening film of fluid would cause a force tending to separate the surfaces.

The mean line or resultant of this force would act through some point O.

This point O does not necessarily coincide with P_1 the point of maximum pressure.

For equilibrium of the surface AB, O will be in the line of the resultant external force urging the surfaces together, otherwise the surface ACD would change its inclination.

The resultant pressure must also be equal to the resultant external force perpendicular to AB (neglecting the obliquity of CD). If the surfaces were free to approach the pressure would adjust itself to the load, for the nearer the surfaces the greater would be the friction and consequent pressure for the same velocity, so that the surfaces would approach until the pressure balanced the load.

As the distance between the surfaces diminished O would change its position, and therefore, to prevent an alteration of inclination, the surface CD must be constrained so that it could not turn round.

It is to be noticed that continuous lubrication between plane surfaces can only take place with continuous motion in one direction, which is the direction of continuous inclination of the surfaces.

With reciprocating motion, in order that there may be continuous lubrication, the surfaces must be other than plane.

15. *Revolving Cylindrical Surface.*

When the moving surface AB is cylindrical and revolving about its axis, the general motion of the film will differ somewhat from what it is with flat surfaces.

Case 5. *Revolving Motion, CD flat and symmetrically placed.*—The surface velocity of AB may be expressed by U as before. The curves of motion found by the same method as in the previous cases are shown in fig. 10.

Fig. 10.

The curves to the right of GH, the shortest distance between the surfaces, will have the same character as those in fig. 9 to the right of C, at which is also the shortest distance between the surfaces.

On the left of GH the curves will be exactly similar to those on the right, only drawn the other way about, so that they are concave towards a section at P_2 in a similar position on the left to that occupied by P_1 on the right.

This is because a uniformly varying motion would carry a quantity of fluid proportional to the thickness of the stratum from right to left, and thus while it would carry more fluid through the sections towards the right than it would carry across GH, necessitating an outward flow from the position P_1 in both directions, the same motion would carry more fluid away from sections towards C than it would supply past GH, thus necessitating an inward flow towards the position P_2.

Since G is in the middle of CD these two actions, though opposite, will be otherwise symmetrical, and

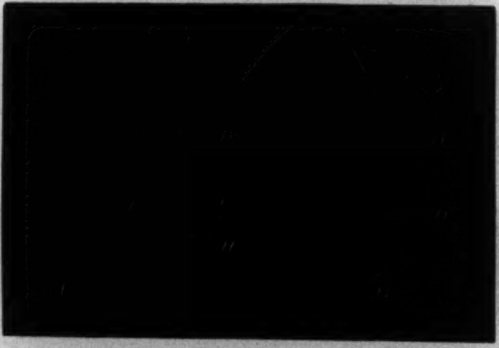
$$P_2G = GP_1.$$

From the convexity of the curves to the section at P_2 it appears that this section would be one of minimum pressure, just as P_1 is of maximum. Of course this is supposing the lubricant under sufficient pressure at C and D to allow of the pressure falling. The curve of pressure would be similar to that at the top of fig. 10, in which C and D are points of equal pressure, P_1HP_2 the singular points in the curve.

Under such conditions the fluid pressure acts to separate the surfaces on the right, but as the pressure is negative on the left the surfaces will be drawn together. So that the total effect will be to produce a turning moment on the surface AB.

Case 6. *The same as Case* 5, *except that G is not in the middle of CD.*—In this case the curves of motion will be symmetrical on each side of H at equal distances, as shown in fig. 11.

Fig. 11.

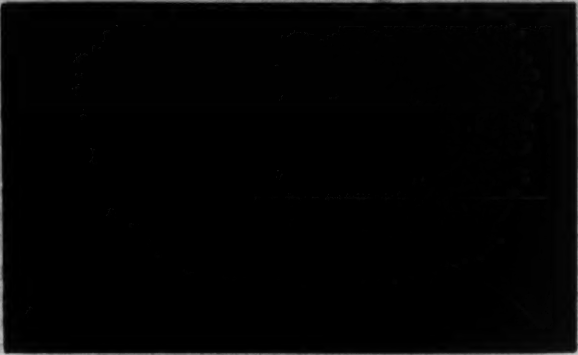


If C lies between H and P_2 the pressure will be altogether positive, as shown by the curve above fig. 11—that is, will tend to separate the surfaces.

16. *The Effect of a Limiting Supply of Lubricating Material.*

In the cases already considered C and D have been the actual limits of the upper surface. If the supply of lubricant is limited C and D may be the extreme points to which the separating film reaches on the upper surface, which may be unlimited, as in fig. 12.

Fig. 12.



Case 7. *Supply of Lubricant Limited.*—If the surface AB be supposed to have been covered with a film of oil, the oil adhering to the surface and moving with it, then the surface CD to have been brought up to a less distance than that occupied by the film of oil, the oil will accumulate as it is brought up by the motion of AB, forming a pad between the surfaces particularly on the side D.

The thickness of the film as it leaves the side C being reduced until the whole surface AB is covered with a film of such thinness that as much leaves at C as is brought up to D, then the condition will be steady.

Putting b for the thickness of the film of oil outside the pad, the quantity of oil brought up to D by the motion of this film will be per second

$$bU,$$

and the quantity which passes the section P_1Q_1, across which the velocity varies uniformly, will be

$$\frac{P_1Q_1U}{2}.$$

Therefore since there is no further accumulation

$$P_1Q_1=2b,$$

also, since $GP_2=GP_1$ (fig. 10, Case 5)

$$P_2Q_2=2b$$

And since the quantity which passes P_2Q_2 will not be sufficient to occupy the larger sections on the left, the fluid will not touch the upper surface to the left of P_2. The limit will therefore be at P_2, the fluid passing away with AB in a film of thickness b.

This is the ordinary case of partial lubrication: AB, the surface of the journal, is covered with a film of oil; CD, the surface of the brass or bearing, is separated from AB by a pad of oil near H, the point of nearest approach.

This pad is under pressure, which is a maximum at P_1, and slopes away to nothing at D and P_2, the extremities of the pad, as is shown by the curve above, fig. 12.

17. *The Relation between Resistance, Load, and Speed for Limited Lubrication.*

In Case 7 a definite quantity of oil must be in the film round the journal, or in the pad between the surfaces. As the surfaces approach the pad will increase and the film diminish, and *vice versâ*. The resistance increases with the length of the pad and with the diminution of the distance between the surfaces. The mean intensity of pressure increases with the length of the pad, and inversely with the thickness of the film, but not in either case in the simple ratio. The total pressure which is equal to the load increases with the intensity of pressure and the length of the pad.

The definite expressions of these relations depend on certain integrations, which have not yet been effected. From the general relations pointed out, it follows that an increase of load will diminish HG and P_1Q_1, and consequently the thickness of the film round the journal, and will increase the length of the pad. It will therefore increase the friction.

Thus with a limited supply of oil the friction will increase with the load in some ratio not precisely determined.

Further, both the friction and the pressure increase in the direct ratio of the speed, provided the distance between the surfaces and the length of the pad remains constant; then, if the load remains constant, the thickness of the film must increase, and the length of the pad diminish with the speed; and both these effects will diminish friction in exactly the same ratio as the reduction of load diminishes friction.

Thus if with a speed U a load W and friction F a certain thickness of oil is maintained, the same will be maintained with a speed MU, a load MW, and the friction will be MF.

How far this increase of friction is to be attributed to the increased velocity, and how far to the increased load, is not yet shown in the theory for this case; but, as has been pointed out, if the load be altered from MW to W, the velocity remaining the same, the friction will be altered from MF in the direction of F. Therefore, with the load constant, it does appear from the theory that the friction will not increase as the first power of the velocity.

There is nothing therefore in this theory contrary to the experience that, with very limited lubrication, the friction is proportional to the load and independent of the velocity, while the theoretical conclusion that the friction, with any particular load and speed, will depend on the supply of oil in the pad, is in strict accordance with Mr. TOWER's conclusion, and with the general disagreement of the coefficients of friction determined in different experiments.

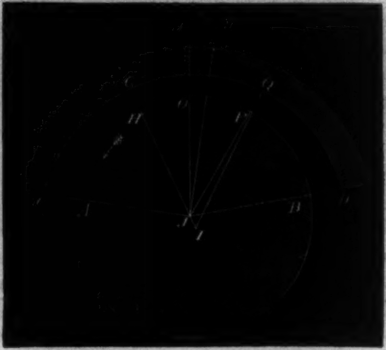
17A. *The Conditions of Equilibrium with Cylindrical Surfaces.*

So far CB has been considered as a flat surface, in which case the equilibrium of CB requires that it should be so far constrained by external forces that it cannot either change its direction or move horizontally.

When AB is a portion of a cylindrical surface, having its axis parallel to that of AB, the only condition of constraint necessary for equilibrium is that CB shall not turn about its axis. This will appear on consideration of the following cases :—

Case 8. *Surfaces Cylindrical and the Supply of Oil Limited.*—Fig. 13 shows the surfaces AB and CD

Fig. 13.



J is the axis of the journal AB.
I is the axis of the brass CD.
JL is the line in which the load acts.
O is the point in which JL meets AB.
R=JP.
R+a=IQ.
h=PQ.
h_0=HG.

The condition for the equilibrium of I is that the resultant of the oil pressure on BC together with friction shall be in the direction OL, and the magnitude of this resultant shall be equal to the load.

As regards the magnitude of this resultant it increases as HG diminishes to a certain limit, *i.e.*, as the surfaces approach, so that in this respect equilibrium is obviously secured, and it is only the direction of the resultant pressure and friction that need be considered.

Since the fluid film is in equilibrium under the forces exerted by the two opposite surfaces these forces must be equal and opposite, so that it is only necessary to consider the forces exerted by AB on the fluid.

From what has been already seen in Cases 6 and 7 it appears that the resultant line of pressure JM always lies on the right or *on* side of GH. The resultant friction clearly acts to the left, so that if JM be taken to represent the resultant pressure and MN the resultant friction, N is to the left of M and JN the resultant of pressure and friction is to the left of JM.

Taking LJ to represent the load, then LN will represent the resultant moving force on CD that is on I. Since H will move in the opposite direction to I, and since the direction of the resultant pressure moves in the same direction as H, the effect of a moving force LN on I will be to move N towards L until they coincide. Thus as long as JM is within the arc covered by the brass a position of equilibrium is possible and the equilibrium will be stable.

So far the condition of equilibrium shows that H will be on the left or off side of the line of load, and this holds whether the supply of oil is abundant or limited; but while with a very limited supply of oil, *i.e.*, a very short oil pad, H must always be in the immediate neighbourhood of O, this is by no means the case as the length of the oil pad increases.

Case 9. *Cylindrical Surfaces in Oil Bath.*—If the supply of oil is sufficient the oil film or pad between the surfaces will extend continuously from the extremities of the brass, unless such extension would cause negative pressure which might lead to discontinuity. In this case the conditions of equilibrium determine the position of H.

The conditions of equilibrium are as before—

1. That the horizontal component of the oil pressure on the brass shall balance the horizontal component of the friction;

2. That the vertical components of the pressure and friction shall balance the load.

Taking the surface of the brass, as is usual, to embrace nearly half the circumference of the journal and, to commence with, supposing the brass to be unloaded, the movement of H may be traced as the load increases.

When there is no load the conditions of equilibrium are satisfied if the position of H is such that the vertical components of pressure and friction are each zero, and the horizontal components are equal and opposite.

This will be when H is at O (fig. 13); for then, as has been shown, Case 5, the pressure on the left of H will be negative, and will be exactly equal to the pressure at corresponding points on the right, so that the vertical components left and right balance each other. On the other hand the horizontal component of the pressure to the left and right will both act on the brass to the right, and as these will increase as the surfaces approach, the distance JI must be exactly such that these components balance the resultant friction, which by symmetry will be horizontal and acting to the left.

It thus appears that when the brass is unloaded its point of nearest approach will be its middle point. This position, together with the curves of pressure, are shown in fig. 14.

Fig. 14.

As the load increases the positive vertical component on the right of GH must overbalance the negative component on the left. This requires that H should be to the left of O.

It is also necessary that the horizontal components of pressure and friction should balance.

These two conditions determine the position of H and the value of JI.

As the load increases it appears from the exact equations (to be discussed in a subsequent article) that OH reaches a maximum value, which places H nearly, but not quite, at the left extremity of the brass, but leaves JI still small as compared with GH.

For a further increase of the load H moves back again towards O.

In this condition the load has become so great that the friction which remains nearly constant is so small by comparison that it may be neglected, and the condition of equilibrium is that the horizontal component of the pressure is zero, and the vertical component equal to the load.

H continues to recede as the load increases. But when HC becomes greater than HP_2, the pressure between P_2 and C would become negative if the condition did not break down by discontinuity in the oil, which is sure to occur when the pressure falls below that of zero, and then the condition becomes the same as that with a limited supply of oil.

This is important, as it shows that with extreme loads the oil bath comes to be practically the same as that of a limited supply of oil, and hence that the extreme load which the brass would carry would be the same in both cases—as Mr. TOWER has shown it to be.

In all Mr. TOWER's experiments with the oil bath it appears that the conditions were such that H was in retreat as the load increased from C towards O, and that, except in the extreme cases, P_2 had not come up to C.

Figs. 2, 3, 4 (Plate 8), show the exact curves of pressure as calculated by the exact method to be given, for circumstances corresponding very closely with one of Mr. TOWER's experiments, in which he actually measured the pressure of oil at three points in the film. These measured pressures are shown by the crosses.

The result of the calculations for this experiment is to show, what could not indeed be measured, that in Mr. TOWER's experiment the difference in the radii of the brass and journal at 70°, and a load of 100 lbs. per square inch,

$$a = \cdot 00077$$

$$GH = \cdot 000375$$

$$\text{(The angle) } OJH = 48^\circ$$

18. *The Wear and Heating of Bearings.*

Before the journal starts the effect of the load will have brought the brass into contact with the journal at O. At starting the surfaces will be in contact, and the initial friction will be between solid surfaces, causing some abrasion.

After motion commences the surfaces gradually separate as the velocity increases, more particularly in the case of the oil bath, in which case at starting the friction will be much the same as with a limited supply of oil.

As the speed increases according to the load, GH approaches, according to the supply of oil, to a, and varies but slightly with any further increase of speed; so that the resistance becomes more nearly proportional to the speed and less affected by the load.

When the condition of steady lubrication has been attained, if the surfaces are completely separated by oil there should be no wear. But if there is wear, as it appears from one cause or another there generally is, it would take place most rapidly where the surfaces are nearest: that is, at GH on the off side of O.

Thus while the motion is in one direction the tendency to wear the surfaces to a fit would be confined to the off side of O.

This appears to offer a very simple and well-founded explanation of the important and common circumstance that new surfaces do not behave so well as old ones; and of the circumstance, observed by Mr. TOWER, that in the case of the oil bath, running the journal in one direction does not prepare the brass for carrying a load when the journal is run in the opposite direction. This explanation, however, depends on the effect of misfit in the journal and brass which has yet to be considered.

Case 10. *Approximately cylindrical surfaces of limited length in the direction of the axis of rotation.*—Nothing has so far been said of any possible motion of the fluid perpendicular to the direction of motion and parallel to the axis of the journal. It having been assumed that the surfaces were truly cylindrical and of unlimited length in direction of their axes, and in such case there would be no such flow.

But in practice brasses are necessarily of limited length, so that the oil can escape from the ends of the brass. Such escape will obviously prevent the pressure of the film of oil from reaching its full height for some distance from the ends of the brass and cause it to fall to nothing at the extreme ends.

This was shown by Mr. TOWER, who measured the pressure at several points along the brass in the line through O, and found it to follow a curve similar to that shown in fig. 15, which corresponds to what might be expected from escape at the free ends.

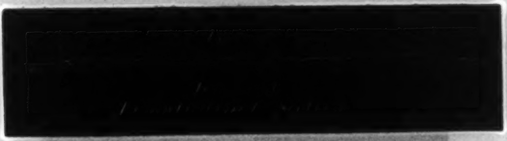
Fig. 15.

If the surfaces are not strictly parallel in the directions TU and VW, the pressure would be greatest in the narrowest parts, causing axial flow from those into the broader spaces. Hence, if the surfaces were considerably irregular, the lubricant would, by escaping into broader spaces, allow the brass to approach and eventually to touch the journal at the narrowest spaces, and this would be particularly the case near the ends.

As a matter of fact, the general fit of two new surfaces can only be approximate; and how near the approximation is, is a matter of the time and skill spent on preparing, or, as it is called, bedding them. Such bedding as brasses are subject to would not bring them to a condition in which the hills and hollows differed by less than a $\frac{1}{10000}$th part of an inch, so that two such surfaces touching each other on the hills would have spaces as great as a $\frac{1}{5000}$th of an inch between them. This seems a small matter, but not when compared with the mean width of the interval between the brass and the journal which, as will be subsequently shown, was less than $\frac{1}{1000}$th of an inch.

It may be assumed, therefore, that such inequalities generally exist in the surfaces of new brasses and journals. And as the surfaces according to their material and manner of support yield to pressure the brass will close on the journal at its ends, where, owing to the escape of oil, there is no pressure to keep them separate.

Fig. 16.



The section of a new brass and journal taken at GH will therefore be, if sufficiently magnified, as shown in fig. 16, the thickness of the film, instead of being, say, of $\frac{3}{10000}$ths of an inch, varies from 0 to $\frac{5}{10000}$ths, and is less at the ends than at the middle.

In this condition the wear will be at the points of contact, which will be in the neighbourhood of GH on the off side of O (fig. 13), so that if the journal runs in one direction only the surfaces in the neighbourhood of GH (on the *off* side) will be gradually worn to a fit, during which wear the friction will be great and attended with heating, more or less, according to the rate of wear and the obstruction to the escape of heat.

So long, however, as the journal runs in one direction only GH will be on one side (the *off* side) of O, and the wear will be altogether or mainly on this side, according to the distance of H from O.

In the meantime the brass on the *on* side is not similarly worn, so that if the motion of the journal is reversed and the point H transferred to the late *on* side the wear will have to be gone through again.

That this is the true explanation is confirmed if, as seems from Mr. TOWER's report, the heating effect on first reversing the journal was much more evident in the case of the oil bath.

For when the supply of oil is short HG will be very small and H will be close to O. So that the wearing area will probably extend to both sides of O, and thus the brass be partially, if not altogether, prepared for running in the opposite direction.

When the supply of oil is complete, however, as has been shown, H is 50° or 60° from O, unless the load is in excess, so that the wear in the neighbourhood of H on the one side of O would not extend to a point 100° or 120° over to the other side.

Even in the case of a perfectly smooth brass the running of the journal under a sufficient load in one direction should, supposing some wear, according to the theory render the brass less well able to carry the load when running in the opposite direction. For, as has already appeared, the pressure between the journal and brass depends on the radius of curvature of the brass on the *on* side being greater than that of the journal. If then the effect of wear is to diminish the radius of the brass on the *off* side, so that when the motion is reversed the radius of the new *on* side is equal to or less than that of the journal, while the radius of the new *off* side is greater, the oil pressure would not rise. And this is the effect of wear; for as will be definitely shown, the effect of the oil pressure is to increase the radius of curvature of the brass, and as the centre of wear is well on the *off* side, the effect of sufficient wear will be to bring the radius on this side, while the pressure is on, more nearly to that of the journal, so that on the pressure being removed the brass on this side may resume a radius even less than that of the journal.

SECTION IV.—THE EQUATIONS OF HYDRODYNAMICS AS APPLIED TO LUBRICATION.

19. According to the usual method of expressing the stress in a viscous fluid (which is the same as in an elastic solid)* :

$$\left.\begin{aligned} p_{xx}&=-p-\tfrac{2}{3}\mu\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)+2\mu\frac{du}{dx}\\ p_{yy}&=-p-\tfrac{2}{3}\mu\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)+2\mu\frac{dv}{dy}\\ p_{zz}&=-p-\tfrac{2}{3}\mu\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)+2\mu\frac{dw}{dz}\end{aligned}\right\} \quad \dots\dots\dots \quad (9)$$

$$\left.\begin{aligned} p_{xy}&=p_{yx}=\mu\left(\frac{dv}{dx}+\frac{du}{dy}\right)\\ p_{yz}&=p_{zy}=\mu\left(\frac{dw}{dy}+\frac{dv}{dz}\right)\\ p_{zx}&=p_{xz}=\mu\left(\frac{du}{dz}+\frac{dw}{dx}\right)\end{aligned}\right\} \quad \dots\dots\dots \quad (10)$$

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* STOKE'S "On the Theories of the Internal Friction of Fluids in Motion, and of the Equilibrium and Motion of Elastic Solids."—Trans. Cambridge Phil. Soc., vol. viii., p. 287. Also reprint, vol. i, p. 84. Also LAMB'S 'Motion of Fluids,' p. 219.

In which the left-hand members are the stresses on plane perpendicular to the first suffix in directions parallel to the second, the first three being the normal stresses, the last six the tangential stresses.

The values of these substituted in the equations of motion

$$\left.\begin{aligned} \rho\frac{\delta u}{\delta t}&=\rho X+\frac{dp_{xx}}{dn}+\frac{dp_{yx}}{dy}+\frac{dp_{zx}}{dz} \\ \rho\frac{\delta v}{dt}&=\rho Y+\frac{dp_{xy}}{dx}+\frac{dp_{yy}}{dy}+\frac{dp_{zy}}{dz} \\ \rho\frac{\delta w}{\delta t}&=\rho Z+\frac{dp_{xz}}{dx}+\frac{dp_{yz}}{dy}+\frac{dp_{zz}}{dz} \\ \frac{\delta\rho}{\delta t}&=\rho\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

give the complete equations of motion for the interior of a viscous fluid.

These equations involve terms severally depending on the inertia and the weight of the fluid, also the variation of stress in the fluid.

In the case of lubrication the spaces between the solid surfaces are so small compared with

$$\frac{\mu}{U}$$

that the motion of the fluid is shown to be free from eddies as already explained (Art. 11). Also that the forces arising from weight and inertia are altogether small compared with the stresses arising from viscosity.

The equations which result from the substitution from (9) and (10) in the first 3 of (11) may therefore be simplified by the omission of the inertia and gravitation terms, which are the terms involving ρ as a factor.

In the case of oil the remaining terms may still further be simplified by omitting the terms depending on the compressibility of the fluid.

Also if, as is the case, μ is nearly constant the terms involving $d\mu$ may be omitted or considered of secondary importance.

From equations (11) we then have

$$\left.\begin{aligned} \frac{dp}{dx}&=\mu\left(\frac{d^2u}{dx^2}+\frac{d^2u}{dy^2}+\frac{d^2u}{dz^2}\right) \\ \frac{dp}{dy}&=\mu\left(\frac{d^2v}{dx^2}+\frac{d^2v}{dy^2}+\frac{d^2v}{dz^2}\right) \\ \frac{dp}{dz}&=\mu\left(\frac{d^2w}{dx^2}+\frac{d^2w}{dy^2}+\frac{d^2w}{dz^2}\right) \\ 0&=\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Again, since in the case of lubrication we always have to do with a film of fluid between nearly parallel surfaces, of which the radii of curvature are large compared with the thickness of the film, we may without error disregard any curvature there may be in the surfaces, and put

x for distances measured on one of the surfaces in the direction of relative motion,

z for distances measured on the same surface in the direction perpendicular to relative motion,

y for distances measured everywhere at right angles to the surface.

Then, if the surfaces remain in their original direction, since they are nearly parallel,

v will be small compared with u and w, and the variations of u and w in the directions x and z are small compared with their variations in the direction y.

The equations (12) for the interior of the film then become

$$\left.\begin{aligned} \frac{dp}{dx}&=\mu\frac{d^2u}{dy^2} \\ \frac{dp}{dy}&=0 \\ \frac{dp}{dz}&=\mu\frac{d^2w}{dy^2} \\ 0&=\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Equations (10) become

$$\left.\begin{aligned} p_{xy}&=p_{yx}=\mu\frac{du}{dy} \\ p_{yz}&=p_{zy}=\mu\frac{dw}{dy} \\ p_{zx}&=p_{xz}=0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

20. The fluid is subject to boundary conditions as regards pressure and velocity. These are—

(1) At the lubricated surfaces the fluid has the velocity of those surfaces;

(2) At the extremities of the surfaces or film the pressure depends on external conditions.

Thus taking the solid surfaces as $y=0$, $y=h$, and as being limited in the direction x and z by the curve

$$f(xy)=0$$

For boundary conditions

$$\left.\begin{array}{llll} y=0 & u=\mathrm{U}_0 & w=0 & v=0 \\ y=h & u=\mathrm{U}_1 & w=0 & v=\mathrm{U}_1\dfrac{dh}{dx}+\mathrm{V}_1 \\ & f(xy)=0 & p=p_0 & \end{array}\right\} \quad . \quad . \quad . \quad (15)$$

21. Equations (13) may now be integrated, the constants being determined by the conditions (15).

The second of these equations gives p independent of y, so that the first and third are directly integrable, whence

$$\left.\begin{aligned} u&=\frac{1}{2\mu}\frac{dp}{dx}(y-h)y+\mathrm{U}_0\frac{h-y}{h}+\mathrm{U}_1\frac{y}{h} \\ w&=\frac{1}{2\mu}\frac{dp}{dz}(y-h)y \end{aligned}\right\} \quad . \quad . \quad . \quad (16)$$

Differentiating these equations with respect to x and z respectively, and substituting in the last of equations (13)

$$\frac{dv}{dy}=-\frac{1}{2\mu}\left[\frac{d}{dx}\left\{\frac{dp}{dx}(y-h)y\right\}+\frac{d}{dz}\left\{\frac{dp}{dz}(y-h)y\right\}\right]-\frac{d}{dx}\left\{\mathrm{U}_0\frac{h-y}{h}+\mathrm{U}_1\frac{y}{h}\right\}$$

Integrating from $y=0$ to $y=h$, and substituting from conditions (15)

$$\frac{d}{dx}\left(h^3\frac{dp}{dx}\right)+\frac{d}{dz}\left(h^3\frac{dp}{dz}\right)=6\mu\left\{(\mathrm{U}_0+\mathrm{U}_1)\frac{dh}{dx}+2\mathrm{V}_1\right\} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

From equations (16) and (14)

$$\left.\begin{aligned} p_{yx}&=\tfrac{1}{2}\frac{dp}{dx}(2y-h)+\mu(\mathrm{U}_1-\mathrm{U}_0)\frac{1}{h} \\ p_{yz}&=\tfrac{1}{2}\frac{dp}{dz}(2y-h) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Putting f_x f_z for the shearing stresses at the solid on the surfaces in the directions x and z respectively, then taking the positive sign when $y=h$, and the negative when $y=0$

$$\left.\begin{aligned} f_x&=\mu(\mathrm{U}_1-\mathrm{U}_0)\frac{1}{h}\mp\tfrac{1}{2}\frac{dp}{dx}h \\ f_z&=\mp\tfrac{1}{2}\frac{dp}{dz}h \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Equations 17 and 19 are the general equations of equilibrium for the lubricant between continuous surfaces at a distance h, where h is any continuous function of x and z, and μ is constant.

22. For the further integration of these equations it is necessary to know the exact manner in which x and z enter into h, as well as the function which determines the limit of lubricated surfaces.

These integrations have been effected either completely or approximately for certain cases, which include the chief case of practical lubrication.

Complete integration has been obtained for the case of two parallel circular or elliptical surfaces approaching without tangential motion. This case is interesting from the experiment, treated approximately by STEFAN,* of one surface-plate floating on another in virtue of the separating film of air. It is introduced here, however, as being the most complete as well as the simplest case in which to consider the important effect of normal motion in the action of lubricants. It corresponds with Case 2, section III.

Complete integration is also obtained for two plane surfaces

$$h=h_1\left(1+m\frac{x}{a}\right)$$

between the limits at which $p=\Pi$ (the pressure of the atmosphere)

$$x=0, \qquad x=a,$$

the surfaces being unlimited in the direction of z. This corresponds with Case 4, section III.

For the most important case, that of cylindrical surfaces, approximate integration has been effected for the case of complete lubrication with the surfaces unlimited in the direction of z. Case 9, section III.

SECTION V.—CASES IN WHICH THE EQUATIONS ARE COMPLETELY INTEGRATED.

23. *Two Parallel Plane Surfaces approaching each other, the Surfaces having Elliptical Boundaries.*

Here h is constant over the surfaces, and when

$$\frac{x^2}{a^2}+\frac{z^2}{c^2}=1, \quad p=\Pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

U_0, U_1 are zero.

Equation (17) becomes

$$\left(\frac{d}{dx^2}+\frac{d}{dz^2}\right)p=\frac{12\mu}{h^3}\frac{dh}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The solution of which is

$$p=\phi(t)\left\{\frac{x^2}{a^2}+\frac{z^2}{c^2}+C_,\right\}+E_1e^{-\frac{z}{a}}\sin\frac{y}{c}+\&c. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

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* Wien. Sitz. Ber., vol. 69 (1874), p. 713.

Therefore

$$2\phi(t)\left(\frac{1}{a^2}+\frac{1}{c^2}\right)=\frac{12\mu}{h^3}\frac{dh}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and

$$E_1=0, \text{ \&c.}$$

$$C_1=-1+\frac{\Pi}{\phi(t)}$$

$$p-\Pi=\frac{12\mu}{h^3}\cdot\frac{a^2c^2}{a^2+c^2}\left\{\frac{x^2}{a^2}+\frac{z^2}{c^2}-1\right\}\frac{dh}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

From equations (19)

$$\left.\begin{aligned} f_x&=\mp\frac{24\mu}{h^3}\,\frac{a^2c^2}{a^2+c^2}\cdot x\,\frac{dh}{dt} \\ f_z&=\mp\frac{24\mu}{h^3}\,\frac{a^2}{a^2+c^2}\cdot z\,\frac{dh}{dt} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

supposing surfaces horizontal and the upper surface supported solely by the pressure of the fluid. The conditions of equilibrium in this case are obvious by symmetry.

The centre of gravity of the load must be vertically over the centre of the ellipse. Since by symmetry

$$\left.\begin{aligned} &\int_0^c\int_0^{a\sqrt{\left(1-\frac{z^2}{c^2}\right)}} px\,dx\,dz=0 \\ &\int_0^c\int_0^{a\sqrt{\left(1-\frac{z^2}{c^2}\right)}} pz\,dx\,dz=0 \\ &\int_0^c\int^{a\sqrt{\left(1-\frac{z^2}{c}\right)}} f_x\,dx\,dz=0 \\ &\int_0^c\int_0^{a\sqrt{\left(1-\frac{z^2}{c}\right)}} f_z\,dx\,dz=0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

And

$$W=\int_0^c\int_0^{a\sqrt{1-\frac{z^2}{c}}} p-\Pi\,dx\,dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

$$=-\frac{3\mu\pi}{h^3}\,\frac{a^3c^3}{a^2+c^2}\cdot\frac{dh}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Therefore integrating

$$t=\frac{3\mu\pi a^3c^3}{(a^2+c^2)W}\left(\frac{1}{{h_2}^2}-\frac{1}{{h_1}^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

t being the time occupied in falling from h_1 to h_2.

24. *Plane Surfaces of unlimited Length and parallel in the Direction of z.*

The lower surface unlimited in the direction x and moving with a velocity $-$U. The upper surface fixed and extending from $x=0$ to $x=a$. This case corresponds with Case 4, Section III.

The boundary conditions are

$$\left.\begin{array}{lll} \left.\begin{array}{l} x=0 \\ x=a \end{array}\right\} & p=\Pi & \\ y=0 & \mathrm{U}_0=-\mathrm{U} & \\ y=h & \mathrm{U}_1=0 & \mathrm{V}_1=0 \\ h=h_0\left(1+m\dfrac{x}{a}\right) & & \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

p is a function of x only.

And from equation (17), Section. IV., by integration

$$\frac{dp}{dx}=-6\mu\mathrm{U}\frac{h-h_1}{h^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

h_1 being the value of h when $x=x_1$ where the pressure is a maximum.

Integrating with respect to x, and putting $p=\Pi$ at the boundaries

$$x_1=\frac{a}{2+m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$p=\Pi+6\frac{\mu\mathrm{U}a}{h^2m}\left\{\frac{1}{1+m\dfrac{x}{a}}-\frac{1+m}{2+m}\,\frac{1}{\left(1+m\dfrac{x}{a}\right)}-\frac{1}{2+m}\right\} \quad . \quad (33)$$

$$\int_0^a(p-\Pi)\,dx=\frac{6\mu\mathrm{U}a^2}{h^2m^2}\left\{\log_e(1+m)-\frac{m}{1+\dfrac{m}{2}}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

or putting W for the load per unit of breadth, W is a maximum when $m=1{\cdot}2$ approximately and

$$\frac{\mathrm{W}}{a}={\cdot}16\mu\mathrm{U}\frac{a^2}{h^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

again, by equation (19)

$$f_x=\mu\frac{\mathrm{U}_1}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

therefore

$$\int_0^a f_x\,dx=\frac{\mu a\mathrm{U}}{h_1m}\log_e(1+m) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and if

$$m=1{\cdot}2$$

$$\mathrm{F}={\cdot}6572\,\frac{\mu a\mathrm{U}}{h_1} \quad . \quad . \quad . \quad . \quad . \quad (38)$$

In order to render the application of equations (35) and (38) clear, a particular case may be assumed.

Let

$$\mu=10^{-5}$$

which is the value for olive oil at a temperature of 70° Fahr., the unit of length being the inch, and that of force the lb.

Let

$$\begin{aligned} \mathrm{U}&=60 \text{ (inches per sec.)} \\ h_1&=\cdot 0003. \end{aligned}$$

Then from (35), the load in lbs. per square inch of lubricated surface is given by

$$\frac{\mathrm{W}}{a}=1070a^2$$

and from 38, the frictional resistance in lbs. per square inch is

$$\frac{\mathrm{F}}{a}=1\cdot 31$$

This seems to be about the extreme case of perfect lubrication between plane metal surfaces having what appears to be about the minimum value of h_1.

SECTION VI.—THE INTEGRATION OF THE EQUATIONS FOR THE CASE OF CYLINDRICAL SURFACES.

25. *General Adaptation of the Equations.*

Fig. 17 represents a section of two circular cylindrical surfaces at right angles to the axes; as in Art. 17

J is the axis of the journal AB;
I is the axis of the brass CD;
JO is the line of action of the load cutting the brass symmetrically, and

$$\left.\begin{aligned} \mathrm{R}&=\mathrm{JP} \\ \mathrm{R}+a&=\mathrm{IQ} \\ h&=\mathrm{PQ} \\ h_0&=\mathrm{HG}, \text{ the smallest section.} \\ \mathrm{JI}&=ca \\ \mathrm{PJO}&=\theta \\ \mathrm{GJO}&=\frac{\pi}{2}-\phi_0 \\ \mathrm{P_1JO}&=\phi_1. \quad \mathrm{P_1} \text{ being the point of maximum pressure.} \end{aligned}\right\} \quad . \quad . \quad . \quad (39)$$

Fig. 17.

Then taking x for distances measured in the direction OA from O on the surface AB, and putting r for the distance of any point from J

$$\left.\begin{aligned} x&=\mathrm{R}\theta \\ y&=r-\mathrm{R} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$x_1=\mathrm{R}\phi_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Neglecting quantities of the order $\overline{\frac{ca}{\mathrm{R}}}\Big|^2$

$$h=a\{1+c\sin(\theta-\phi_0)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

For if I be moved up to J, Q moves through a distance ca in the direction JH.

The boundary conditions are such that

(1) all quantities are independent of z

(2) U_0 is constant, U_1 and $\mathrm{V}_1=0$

(3) putting $\theta_0=\mathrm{OJA}$, $\theta_1=\mathrm{OJB}$, whence by symmetry $\theta_0=-\theta_1$

$$\left.\begin{aligned} \theta&=\theta_0 \\ \theta&=\theta_1 \end{aligned}\right\} \ldots p=p_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Putting $-L$ for the effect of the external load and $-M$ for the external moment per unit of length in the direction z, and assuming that there are no external horizontal forces, the conditions of equilibrium for the brass are

$$\int_{\phi_0}^{\phi_1}\{p\sin\theta-f\cos\theta\}d\theta=0 \quad \ldots\ldots\ldots \quad (44)$$

$$\int_{\phi_0}^{\phi_1}\{p\cos\theta+f\sin\theta\}d\theta=\frac{L}{R} \quad \ldots\ldots\ldots \quad (45)$$

$$\int_{\phi_0}^{\phi} fd\theta=\frac{M}{R^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (46)$$

Substituting from equations (40) (41) (42) in equations (17) and (19), Section IV., putting

$$K_1=\frac{6R\mu U_0}{a^2}, \qquad K_2=\frac{\mu U_0}{a} \quad \ldots\ldots\ldots \quad (47)$$

and remembering the boundary conditions, these equations become on integration

$$\frac{dp}{d\theta}=\frac{6R\mu U_0 c\{\sin(\theta-\phi_0)-\sin(\phi_1-\phi_0)\}}{a^2\{1+c\sin(\theta-\phi_0)\}^3} \quad \ldots\ldots\ldots \quad (48)$$

$$f=-\frac{3\mu U_0 c\{\sin(\theta-\phi_0)-\sin(\phi_1-\phi_0)\}}{a\{1+c\sin(\theta-\phi)\}^2}$$

$$-\frac{\mu U_0}{\{1+c\sin(\theta-\phi)\}} \quad \ldots\ldots\ldots\ldots\ldots \quad (49)$$

26. *The Method of Approximate Integration.*

The second numbers of equations (48) and (49) may be expanded so that

$$\left.\begin{aligned}\frac{1}{K_1c}\frac{dp}{d\theta}=A_0+A_1\sin(\theta-\phi_0)+A_2\cos2(\theta-\phi)+, \&c.\\ +A_{2n}\cos2x(\theta-\phi_0)+A_{2n+1}\sin\{(2x+1)(\theta-\phi)\}\end{aligned}\right\} \quad \ldots\ldots \quad (50)$$

$$\left.\begin{aligned}-\frac{1}{K_2}f=B_0+B_1\sin(\theta-\phi_0)+B_2\cos2(\theta-\phi)+\ \&c.\\ +B_{2n}\cos2x(\theta-\phi)+B_{2n+1}\sin\{(2x+1)(\theta-\phi)\}\end{aligned}\right\} \quad \ldots\ldots \quad (51)$$

Putting

$$\chi=\sin(\phi_1-\phi_0) \quad \ldots\ldots\ldots\ldots \quad (52)$$

$$
\left.\begin{aligned}
A_0 &= -\chi-\Sigma_{r=2}^{r=2\infty}\left\{\frac{(r+1)r^2(r-1)\ldots\frac{r+2}{2}}{2^{r+1}\underline{|\frac{r}{2}}}c^{r-1}+\frac{(r+2)(r+1)r(r-1)\ldots\frac{r+2}{2}}{2^{r+1}\underline{|\frac{r}{2}}}c^r\chi\right\}\\
A_{2n} &= (-1)^{n+1}\left\{\frac{(2n+1)2n}{2^{2n}}c^{2n+1}+\frac{(2n+2)(2n+1)}{2^{2n}}c^{2n}\chi\right.\\
&\qquad\left.+\Sigma_{r=2n+2}^{r=2\infty}\left[\frac{(r+1)r^2(r-1)\ldots\frac{r+2n+2}{2}}{2^r\underline{|\frac{r}{2}-n}}c^{r-1}+\frac{(r+2)(r+1)r\ldots\frac{r+2n+2}{2}}{2^r\underline{|\frac{r}{2}-n}}c^r\chi\right]\right\}\\
A_{2n+1} &= (-1)^n\left\{\frac{(2n+2)(2n+1)}{2^{2n+1}}c^{2n}+\frac{(2n+3)(2n+2)}{2^{2n+1}}c^{2n+1}\chi\right.\\
&\qquad\left.+\Sigma_{r=2n+3}^{r=2\infty+1}\left[\frac{(r+1)r^2(r-1)\ldots\frac{r+2n+3}{2}}{2^r\underline{|\frac{r-2n-1}{2}}}c^{r-1}+\frac{(r+2)(r+1)r\ldots r+2n+2}{2^r\underline{|\frac{r-2n-1}{2}}}c^r\chi\right]\right\}
\end{aligned}\right\}\tag{53}
$$

$$
\left.\begin{aligned}
B_0 &= 1-3c\chi+\Sigma_{r=2}^{r=2\infty}\left[\frac{(4-3(r+1))r.(r-1)\ldots\frac{r+2}{2}}{2^r\underline{|\frac{r}{2}}}c^r\right.\\
&\qquad\left.\left.-\frac{3(r+1)r(r-1)\ldots\frac{r+1}{2}}{2^r\underline{|\frac{r}{2}}}c^{r+1}\chi\right]\right\}\\
B_{2n} &= (-1)^n\left\{\frac{[4-3(2n+1)]c^{2n}-3(2n+1)c^{2n+1}\chi}{2^{2n-1}}\right.\\
&\qquad\left.+\Sigma_{r=2n+2}^{r=2\infty}\Big[[4-3(r+1)]c^r-3(r+1)c^{r+1}\chi\Big]\frac{r.(r-1)\ldots\frac{r+2n+2}{2}}{2^{r-1}\underline{|\frac{r-2n}{2}}}\right\}\\
B_{2n+1} &= (-1)^{n+1}\left\{\frac{[4-3(2n+2)]c^{2n+1}-3(2n+2)c^{2n+2}\chi}{2^{2n}}\right.\\
&\qquad\left.+\Sigma_{r=2n+3}^{r=2\infty+3}\Big[[4-3(r+1)]c^r-3(r+1)c^{r+1}\chi\Big]\frac{r.(r+1)\ldots r+2n+3}{2^{r-1}\underline{|\frac{r-2n-1}{2}}}\right\}
\end{aligned}\right\}\tag{54}
$$

The coefficients A_0, A_1, &c., B_0, B_1, &c., are thus expanded in a series of ascending powers of c with numerical coefficients which do not converge. It seems, however, that if c is not greater than ·6 the series are themselves convergent, and it is only necessary to go to the tenth or twelfth term, to which extent they have been calculated, and are as follows :—

$$\left.\begin{aligned}
A_0 &= -1\cdot 5c - 3\cdot 75c^3 - 6\cdot 565c^5 - 9\cdot 85c^7 - 13\cdot 51c^9 - 17\cdot 6c^{11} \\
&\qquad - \{1 + 3c^2 + 5\cdot 625c^4 + 8\cdot 75c^6 + 12\cdot 225c^8 + 16\cdot 2c^{10}\}\chi \\
A_1 &= 1 + 4\cdot 5c^2 + 9\cdot 375c^4 + 15\cdot 23c^6 + 21\cdot 92c^8 + 29\cdot 8c^{10} + 38\cdot 6c^{12} \\
&\qquad + \{3c + 7\cdot 5c^3 + 13\cdot 13c^5 + 19\cdot 7c^7 + 27\cdot 01c^9 + 35\cdot 2c^{11}\}\chi \\
A_2 &= 1\cdot 5c + 5c^3 + 9\cdot 85c^5 + 15\cdot 75c^7 + 22\cdot 56c^9 + 20\cdot 24c^{11} \\
&\qquad + \{3c^2 + 7\cdot 5c^4 + 13\cdot 13c^6 + 19\cdot 7c^8 + 27\cdot 02c^{10} + 35\cdot 2c^{12}\}\chi \\
A_3 &= -1\cdot 5c^2 - 4\cdot 7c^4 - 9\cdot 2c^6 - 14\cdot 7c^8 - 21\cdot 45c^{10} \\
&\qquad - \{2\cdot 5c^3 + 6\cdot 56c^5 + 11\cdot 78c^7 + 18\cdot 03c^9 + 25\cdot 4c^{11}\}\chi \\
A_4 &= -1\cdot 25c^3 - 3\cdot 94c^5 - 7\cdot 875c^7 - 12\cdot 88c^9 - 18\cdot 8c^{11} \\
&\qquad - \{1\cdot 875c^4 + 5\cdot 25c^6 + 9\cdot 85c^8 + 15\cdot 48c^{10} + 22\cdot 45c^{12}\}\chi \\
A_5 &= \cdot 939c^4 + 3\cdot 07c^6 + 6\cdot 33c^8 + 10\cdot 68c^{10} \\
&\qquad + \{2\cdot 63c^5 + 3\cdot 94c^7 + 7\cdot 76c^9 + 12\cdot 6c^{11}\}\chi
\end{aligned}\right\} \quad . \quad (55)$$

$$\left.\begin{aligned}
B_0 &= 1 - \{2\cdot 5c^2 + 4\cdot 125c^4 + 5\cdot 3125c^6 + 6\cdot 54c^8\} \\
&\qquad - \{3c + 4\cdot 5c^3 + 5\cdot 625c^5 + 6\cdot 562c^7 + 7\cdot 63c^9\}\chi \\
B_1 &= 2c + 6c^3 + 9\cdot 75c^5 + 11\cdot 3125c^7 \\
&\qquad + \{6c^2 + 9c^4 + 11\cdot 25c^6 + 12\cdot 5c^8\}\chi \\
B_2 &= 2\cdot 5c^2 + 5\cdot 5c^4 + 7\cdot 97c^6 + 10\cdot 06c^8 \\
&\qquad + \{4\cdot 5c^3 + 7\cdot 5c^5 + 9\cdot 85c^7 + 11\cdot 8c^9\}\chi \\
B_3 &= -2c^3 - 4\cdot 375c^5 - 6\cdot 5625c^7 - 8\cdot 61c^9 \\
&\qquad - \{3c^4 + 5\cdot 625c^6 + 7\cdot 873c^8 + 9\cdot 84c^{10}\}\chi \\
B_4 &= -1\cdot 375c^4 - 3\cdot 2c^6 - 5\cdot 03c^8 \\
&\qquad - \{1\cdot 875c^5 + 3\cdot 94c^7 + 5\cdot 09c^9\}\chi
\end{aligned}\right\} \quad . \quad . \quad . \quad (56)$$

27. *The Integration of the Equations.*

Integrating equation (50) between the limits θ_0 and θ

$$\begin{aligned}\frac{p-p_0}{\mathrm{K}_1c}=\mathrm{A}_0(\theta-\theta_0)&\\ -\mathrm{A}_1\{\cos(\theta-\phi_0)-\cos(\theta_0-\phi_0)\}&\\ +\frac{\mathrm{A}_2}{2}\{\sin 2(\theta-\phi_0)-\sin 2(\theta_0-\phi_0)\}&\\ \&\text{c.}\qquad\qquad \&\text{c.}&\\ -\frac{\mathrm{A}_{2n+1}}{2n+1}\{\cos[(2n+1)(\theta-\phi_0)]-\cos[(2n+1)(\theta_0-\phi_0)]\}&\\ +\frac{\mathrm{A}_{2n}}{2n}\{\sin 2n(\theta-\phi_0)-\sin 2n(\theta_0-\phi_0)\}&\ .\ .\ .\ .\ .\ .\ .\ . \quad (57)\end{aligned}$$

whence putting $\theta=\theta_1$ by condition (43)

$$\begin{aligned}0=\mathrm{A}_0\theta_1-\mathrm{A}_1\sin\theta_1\sin\phi_0+\frac{\mathrm{A}_2}{2}\sin 2\theta_1\cos 2\phi_0-,\ \&\text{c.}&\\ -\frac{\mathrm{A}_{2n+1}}{2n+1}\sin[(2n+1)\theta_1]\sin(2n+1)\phi_0&\\ +\frac{\mathrm{A}_{2n}}{2n}\sin 2n\theta_1\cos 2n\phi_0&\ .\ .\ .\ .\ .\ .\ .\ .\ .\ . \quad (58)\end{aligned}$$

Putting

$$\begin{aligned}\mathrm{E}=\mathrm{A}_1\cos\theta_1\cos\phi_0+\frac{\mathrm{A}_2}{2}\cos 2\theta_1\sin 2\phi_0+,\ \&\text{c.}&\\ +\frac{\mathrm{A}_{2n+1}}{2n+1}\cos[(2n+1)\theta_1]\cos[(2n+1)\phi_0]&\\ +\frac{\mathrm{A}_{2n}}{2n}\cos 2n\theta_1\sin 2n\phi_0&\ .\ .\ .\ .\ .\ .\ .\ .\ .\ . \quad (59)\end{aligned}$$

whence from equations (57) and (58)

$$\begin{aligned}\frac{p-p_0}{\mathrm{K}_1c}=\mathrm{E}+\mathrm{A}_0\theta-\mathrm{A}_1\cos(\theta-\phi_0)+\frac{\mathrm{A}_2}{2}\sin 2(\theta-\phi_0)&\\ -\frac{\mathrm{A}_{2n+1}}{2n+1}\cos[(2n+1)(\theta-\phi_0)]&\\ +\frac{\mathrm{A}_{2n}}{2n}\sin 2n(\theta-\phi_0)&\ .\ .\ .\ .\ .\ .\ .\ .\ .\ . \quad (60)\end{aligned}$$

Multiplying equation (60) by $\sin\theta$ and integrating between θ_0 and θ_1, remembering that $\theta_0 = -\theta_1$

$$\begin{aligned}
\int_{\theta_0}^{\theta_1} \frac{p-p_0}{\mathrm{K}c} \sin\theta d\theta = {} & 2\mathrm{A}_0(\sin\theta_1 - \theta_1\cos\theta_1) \\
& + \mathrm{A}_1\left(\frac{\sin 2\theta_1 \sin\phi_0}{2} - \theta_1 \sin\phi_0\right) \\
& + \frac{\mathrm{A}_2}{2}\left(\sin\theta\cos 2\phi - \frac{\sin 3\theta\cos 2\phi}{3}\right) \\
& \qquad \&\text{c.} \qquad\qquad \&\text{c.} \\
& + \frac{\mathrm{A}_{2n+1}}{2n+1}\left\{\frac{\sin(2n+2)\theta_1 \sin(2n+1)\phi_0}{2n+2} - \frac{\sin 2n\theta_1 \sin(2n+1)\phi_0}{2n}\right\} \\
& \frac{\mathrm{A}_{2n}}{2n}\left\{\frac{\sin(2n+1)\theta_1 \cos 2n\phi}{2n-1} - \frac{\sin(2n+1)\theta\cos 2n\phi}{2n+1}\right\} \quad . \quad . \quad . \quad . \quad (61)
\end{aligned}$$

Multiplying equation (60) by $\cos\theta$, and integrating from θ_0 to θ_1

$$\begin{aligned}
\int_{\theta_0}^{\theta_1} \frac{p-p_0}{\mathrm{K}c}\cos\theta d\theta = {} & -\mathrm{A}_1\left(\theta_1\cos\phi_0 - \frac{\sin 2\theta_1}{2}\cos\phi_0\right) + \frac{\mathrm{A}_2}{2}\left(\frac{\sin 3\theta_1}{6}\sin 2\phi_0 - \tfrac{3}{2}\sin\theta\sin 2\phi\right) - \&\text{c.} \\
& + \frac{\mathrm{A}_{2n+1}}{2n+1}\left\{\frac{2n+1}{2n+2}\sin(2n+2)\theta\cos(2n+1)\phi - \frac{2n+1}{2n}\sin 2n\theta_1\cos(2n+1)\phi\right\} \\
& + \frac{\mathrm{A}_{2n}}{2n}\left\{\frac{2n}{2n+1}\sin(2n+1)\theta\sin 2n\phi - \frac{2n}{2n-1}\sin(2n-1)\theta\sin 2n\phi\right\}. \quad . \quad (62)
\end{aligned}$$

Multiplying equation (51) by $\cos\theta$ and integrating

$$\begin{aligned}
-\int_{\theta_0}^{\theta} \frac{f\cos\theta}{\mathrm{K}_2} = {} & 2\mathrm{B}_0\sin\theta_1 - \mathrm{B}_1\left(\frac{\sin 2\theta_1 \sin\phi_0}{2} + \theta_1\sin\phi_0\right) \\
& + \mathrm{B}_2\left(\frac{\sin 3\theta_1\cos 2\phi_0}{3} + \sin\theta_1\cos 2\phi_0\right) \\
& - \&\text{c.} \\
& + \mathrm{B}_{2n}\left\{\frac{\sin(2n+1)\theta_1\cos 2n\phi_0}{2n+1} + \frac{\sin(2n-1)\theta_1\cos 2n\phi_0}{2n-1}\right\} \\
& - \mathrm{B}_{2n+1}\left\{\frac{\sin(2n+2)\theta_1\sin(2n+1)\phi_0}{2n+2} + \frac{\sin 2n\theta_1\sin(2n+1)\phi_0}{2n}\right\} \quad . \quad . \quad (63)
\end{aligned}$$

Multiplying equation (51) by sin θ and integrating

$$-\int_{\theta_0}^{\theta_1}\frac{f\sin\theta d\theta}{\mathrm{K}_2}=\mathrm{B}_1\left(\frac{\sin 2\theta_1\cos\phi_0}{2}-\theta_1\cos\phi_0\right)-\mathrm{B}_2\left(\frac{\sin 3\theta_1\sin 2\phi_0}{3}-\sin\theta_1\sin 2\phi_0\right)$$

$$-\mathrm{B}_{2n}\left\{\frac{\sin(2n+1)\theta_1\sin 2n\phi_0}{2n+1}-\frac{\sin(2n-1)\theta_1\sin 2n\phi_0}{2n-1}\right\}$$

$$+\mathrm{B}_{2n+1}\left\{\frac{\sin(2n+2)\theta_1\cos(2n+1)\phi_0}{2n+2}\quad\frac{\sin 2n\theta_1\cos(2n-1)\phi}{2n}\right\}\quad .\quad .\quad .\quad (64)$$

Integrating equation (51)

$$-\int_{\theta_0}^{\theta_1}\frac{fd\theta}{\mathrm{K}_2}=2\mathrm{B}_0\theta_1-2\mathrm{B}_1\sin\theta_1\sin\phi_0+\frac{2\mathrm{B}_2}{2}\sin 2\theta_1\cos 2\phi_0$$

$$+\frac{2\mathrm{B}_{2n}}{2n}\sin 2n\theta_1\cos 2n\phi_0$$

$$-\frac{2\mathrm{B}_{2n+1}}{2n+1}\sin(2n+1)\theta_1\sin(2n+1)\phi_0\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (65)$$

Substituting from equations (61)–(65) in the equations of equilibrium (44), (45), (46), there results—

From (44)

$$0=2(\mathrm{K}_1c\mathrm{A}_0+\mathrm{K}_2\mathrm{B}_0)\sin\theta_1-2\mathrm{K}_1c\mathrm{A}_0\theta_1\cos\theta_1$$

$$+(\mathrm{K}_1c\mathrm{A}_1-\mathrm{K}_2\mathrm{B}_1)\frac{\sin 2\theta_1}{2}\sin\phi_0-(\mathrm{K}_1c\mathrm{A}_1+\mathrm{K}_2\mathrm{B}_1)\theta_1\sin\phi_0$$

$$+\ \&\mathrm{c}.$$

$$+\Sigma_{n=1}^{n=\infty}\left\{\left(\frac{\mathrm{K}_1c\mathrm{A}_{2n}}{2n}+\mathrm{K}_2\mathrm{B}_{2n}\right)\frac{\sin(2n-1)\theta_1\cos 2n\phi_0}{2n-1}\right.$$

$$-\left(\frac{\mathrm{K}_1c\mathrm{A}_{2n}}{2n}-\mathrm{K}_2\mathrm{B}_{2n}\right)\frac{\sin(2n+1)\theta_1\cos 2n\phi_0}{2n+1}$$

$$-\left(\frac{\mathrm{K}_1c\mathrm{A}_{2n+1}}{2n+1}+\mathrm{K}_2\mathrm{B}_{2n+1}\right)\frac{\sin 2n\theta_1\sin(2n+1)\phi_0}{2n}$$

$$\left.+\left(\frac{\mathrm{K}_1c\mathrm{A}_{2n+1}}{2n+1}-\mathrm{K}_2\mathrm{B}_{2n+1}\right)\frac{\sin(2n+1)\theta_1\sin(2n+1)\phi_0}{2n+2}\right\}\quad .\quad .\quad .\quad (66)$$

From (45)

$$\frac{\mathrm{L}}{\mathrm{R}}=(\mathrm{K}_1c\mathrm{A}_1-\mathrm{K}_2\mathrm{B}_1)\left(\frac{\sin 2\theta_1}{2}-\theta_1\right)\cos\phi_0$$

$$+\Sigma_{n=1}^{n=\infty}\left\{(\mathrm{K}_1c\mathrm{A}_{2n}+\mathrm{K}_2\mathrm{B}_{2n})\left[\frac{\sin(2n+1)\theta_1}{2n+1}-\frac{\sin(2n-1)\theta_1}{2n-1}\right]\sin 2n\phi_0\right.$$

$$\left.+(\mathrm{K}_1c\mathrm{A}_{2n+1}-\mathrm{K}_2\mathrm{B}_{2n+1})\left[\frac{\sin(2n+2)\theta_1}{2n+2}-\frac{\sin 2n\theta_1}{2n}\right]\cos(2n+1)\phi_0\right\}\quad .\quad (67)$$

From (46)

$$\begin{aligned}-\frac{M}{R^2}=K_2\Big\{&2B_0\theta_1-2B_1\sin\theta_1\sin\phi_0+\frac{2B_2}{2}\sin 2\theta_1\cos 2\phi_0\\&+\frac{2B_{2n}}{2n}\sin 2n\theta_1\cos 2n\phi_0\\&-\frac{2B_{2n+1}}{2n+1}\sin(2n+1)\theta_1\sin(2n+1)\phi_0\Big\}\quad\dots\dots\quad(68)\end{aligned}$$

The equations (66), (67), (68), together with (58), which expresses the boundary conditions as regards pressure, are the integral equations of equilibrium for the fluid between the brass and journal, and hence for the brass.

The quantities involved in these equations are

$$R,\ U,\ M,\ L,\ \mu,\ \theta_1 \quad\text{and}\quad a,\ c,\ \phi_0,\ \phi_1.$$

If, therefore, the former are given, the latter are determined by the solution of these equations.

SECTION VII.—SOLUTION OF THE EQUATIONS FOR CYLINDRICAL SURFACES.

28. *c and* $\sqrt{\frac{a}{R}}$ *small compared with Unity.*

In this case equations (55) become

$$\left.\begin{array}{ll}A_0=-\chi & B_0=1\\A_1=\ \ 1 & B_1=0\\A_2=\ \ 0,\ \&c. & B_2=0,\ \&c.\end{array}\right\}\quad\dots\dots\quad(69)$$

Equation (58) gives

$$0=\chi\theta_1+\sin\theta_1\sin\phi_0\quad\dots\dots\quad(70)$$

Equation (66) gives

$$0=(2K_1c\chi-2K_2)\sin\theta_1-2K_1c\chi\theta_1\cos\theta_1-K_1c\frac{\sin 2\theta_1}{2}\sin\phi_0+K_1c\theta_1\sin\phi_0.\quad(71)$$

Equation (67) gives

$$\frac{L}{R}=K_1c\left(\frac{\sin 2\theta_1}{2}-\theta_1\right)\cos\phi_0\quad\dots\dots\quad(72)$$

and equation (68) gives

$$\frac{M}{R^2}=-2K_2\theta_1\quad\dots\dots\quad(73)$$

Also equation (57)

$$p-p_0=K_1c\{\cos\theta_1\cos\phi_0-\chi\theta-\cos(\theta-\phi)\}\quad\dots\dots\quad(74)$$

Eliminating χ between equations (70) and (71)

$$\sin\phi_0=\frac{K_2}{K_1}\frac{2\sin\theta_1}{c\left(\theta-\dfrac{2\sin^2\theta_1}{\theta_1}+\frac{1}{2}\sin 2\theta\right)}\quad\ldots\ldots\ldots\quad(75)$$

The equations (74) and (75) suffice to determine a, c, ϕ_1 and ϕ_0 under the conditions $\sqrt{\frac{a}{R}}$ and c small so long as ϕ_0 is not small, in which case the terms retained in the equations become so small that some that have been neglected rise into relative importance.

To commence with let

$$L=0$$

(Cases 5 and 9, Section III.)

Then by (72)

$$\cos\phi_0=0$$

and by (70)

$$\chi=-\frac{\sin\theta_1}{\theta_1}$$

putting for χ its value $\sin(\phi_1-\phi_0)$

$$\cos\phi_1=\frac{\sin\theta_1}{\theta_1}\quad\ldots\ldots\ldots\ldots\ldots\quad(76)$$

Equation (76) gives two equal values of opposite signs for ϕ_1. These correspond to the positions of P_1 and P_2, the points of maximum and minimum pressure.

For the extreme cases

$$\left.\begin{array}{ll}\theta_1=0 & \phi_1=\pm\sqrt{\tfrac{2}{3}}\theta_1\\ \theta_1=\dfrac{\pi}{2} & \phi_1=\pm\cos^{-1}\dfrac{2}{\pi}\\ \theta_1=\pi & \phi=0_1\end{array}\right\}\quad\ldots\ldots\ldots\quad(77)$$

From equations (73) and (47)

$$a=\frac{2\mu U\theta}{M}\quad\ldots\ldots\ldots\ldots\ldots\quad(78)$$

and from (75)

$$c=\frac{a}{3R}\frac{\sin\theta_1}{\left(\theta_1-\dfrac{2\sin^2\theta_1}{\theta_1}+\frac{1}{2}\sin 2\theta_1\right)}\quad\ldots\ldots\ldots\quad(79)$$

When L increases

From (72) and (75)

$$\tan\phi_0=\frac{R}{L}K_2\left(\frac{\sin 2\theta_1}{2}-\theta_1\right)\frac{2\sin\theta_1}{\left(\theta_1-\dfrac{2\sin^2\theta_1}{\theta_1}+\frac{1}{2}\sin 2\theta_1\right)}\quad\ldots\ldots\quad(80)$$

Hence as L increases $\tan\phi_0$ diminishes until the approximation fails. This, however, does not happen so long as c is small.

As the load increases from zero, equation (80) shows that G moves away from O towards A.

It also appears from equation (70) that χ and ϕ_1 diminish as ϕ_0 diminishes, and that ϕ_1 is positive as long as the equations hold.

To proceed further it is necessary to retain all terms of the first order of small quantities.

Retaining the first power of c only, equations (55) become

$$\left.\begin{array}{ll} A_0 = -1\cdot5c - \chi & B_0 = 1 - 3c\chi \\ A_1 = 1 + 3c\chi & B_1 = 2c \\ A_2 = 1\cdot5c & B_2 = 0 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

From (58)

$$\chi(\theta_1 + 3c \sin\theta_1 \sin\phi_0) = -\sin\theta_1 \sin\phi_0 - 1\cdot5c\theta_1 + 1\cdot5c\frac{\sin 2\theta_1}{2}\cos 2\phi_0 \quad . \quad . \quad (82)$$

From (66)

$$\begin{aligned} 0 = \{&-2K_1c(1\cdot5c+\chi) + 2K_2(1-3c\chi)\}\sin\theta_1 \\ &+ 2K_1c(1\cdot5c+\chi)\theta_1\cos\theta_1 \\ &+ \{K_1c(1+3c\chi) - 2K_2c\}\frac{\sin 2\theta_1}{2}\sin\phi_0 \\ &- \{K_1c(1+3c\chi) + 2K_2c\}\theta_1\sin\phi_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (83) \\ &+ \tfrac{3}{4}K_1c^2\left(\sin\theta_1 - \frac{\sin 3\theta_1}{3}\right)\cos 2\phi_0 \end{aligned}$$

From (67)

$$\begin{aligned} \frac{L}{R} = -\{K_1c(1+3c\chi) - 2K_2c\}\left(\theta_1 - \frac{\sin 2\theta_1}{2}\right)\cos\phi_0 \\ + K_1c\frac{1\cdot5c}{4}\left(\tfrac{1}{3}\sin 3\theta_1 \sin 2\phi_0 - \sin\theta_1 \sin 2\phi_0\right) \quad . \quad (84) \end{aligned}$$

From (68)

$$\frac{M}{R^2} = -K_2\{2(1-3c\chi)\theta_1 - 4c\sin\theta_1\sin\phi_0\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

In the equations (82) to (85) terms have been retained as far as the second power of c, but these terms have very unequal values. As χ and $\sin\phi_0$ diminish c increases, and the products of $c\chi$ or $c\sin\phi_0$ may be regarded as never becoming important and be omitted when multiplied by K_1c or K_2.

Making such omissions and eliminating χ between (82) and (83)

$$\sin\phi_0 = \frac{\dfrac{2K_2}{K_1c}\theta_1\sin\theta_1 + c\left\{\tfrac{3}{4}\theta_1\left(\sin\theta_1 - \dfrac{\sin 3\theta_1}{3}\right) - 3(\sin\theta_1 - \theta_1\cos\theta_1)\dfrac{\sin 2\theta_1}{2}\right.}{\theta_1\left(\theta_1 - \dfrac{\sin 2\theta_1}{2}\right) - 2(\sin\theta_1 - \theta_1\cos\theta_1)\sin\theta_1} \quad . \quad . \quad (86)$$

Equation (86) is a quadratic for c in terms of $\sin \phi_0$, from which it is clear that as c increases from zero ϕ_0 goes through a minimum value when

$$c^2 = \frac{2K_2}{K_1} \frac{\theta_1 \sin \theta_1}{\frac{3}{4}\theta_1\left(\sin \theta_1 - \frac{\sin 3\theta_1}{3}\right) - 3(\sin \theta_1 - \theta_1 \cos \theta_1)\frac{\sin 2\theta_1}{2}} \quad . \quad . \quad . \quad . \quad (87)$$

As the load increases from zero the value of c increases from that of equation (79) to the positive root of (87). As the load continues to increase c further increases, but ϕ_0 again increases, so that, as shown by equation (86), for values of ϕ_0 greater than the minimum there are two loads, two values of c, and two values of χ.

If θ_1 is nearly $\frac{\pi}{2}$ c will be of the order $\sqrt{\frac{a}{2R}}$ when ϕ_0 is small, and $\sin \phi_0$ will be of the order $4c$; so that, so long as $\sqrt{\frac{a}{2R}}$ is sufficiently small, no error has been introduced by the neglect of products and squares of these quantities.

For example

$$\theta_1 = 1{\cdot}37045 \text{ (78° 31′ 30″ as in TOWER's experiments)} \quad . \quad . \quad . \quad . \quad (88)$$

By equation (86)

$$\sin \phi_0 = 3{\cdot}934c + 1{\cdot}9847 \frac{a}{cR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

And by (87) at the minimum value of ϕ_0

$$\left.\begin{aligned} c &= \sqrt{\frac{a}{2R}} \\ \sin \phi_0 &= 5{\cdot}61 \sqrt{\frac{a}{R}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (90)$$

Putting $\chi = \sin \phi_1 - \sin \phi_0$ equation (82) becomes

$$\sin \phi_1 = -{\cdot}16776c + {\cdot}5656 \frac{a}{Rc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

or, when ϕ_0 is a minimum,

$$\sin \phi_1 = {\cdot}682 \sqrt{\frac{a}{R}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (92)$$

Therefore

$$\chi = 4{\cdot}928 \sqrt{\frac{a}{R}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (93)$$

Equations (84) and (85) give

$$\frac{L}{R} = -1{\cdot}1753 K_1 c \quad . \quad . \quad . \quad . \quad . \quad . \quad (94)$$

$$\frac{M}{R^2} = -2{\cdot}74 K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

whence equations (47)

$$c = \cdot 388 a \frac{L}{M} \quad \text{. . . . . (96)}$$

$$\frac{\mu}{a} = -\cdot 3635 \frac{M}{R^2 U_0} \quad \text{. . . . . (97)}$$

So long then as $a\frac{L}{M}$ is not greater than 0·2, these approximate solutions are sufficiently applicable to any case.

For greater values of $\frac{L}{M}$ the solution becomes more difficult, as long however as c is not greater than ·5 the solution can be obtained for any particular value of c.

29. *Further Approximation to the Solution of the Equations for particular Values of c.*

The process here adopted is to assume a value for c. From equations (53) and (54) to find

$$\begin{array}{ll} A_0 = A_0' + A_0''\chi & B_0 = B_0' + B_0''\chi \quad \text{. . . . . (98)} \\ \&c. & \&c. \end{array}$$

where A_1' A_1'' B_1' B_1'' are numerical.

These coefficients are then introduced into equations (58) and (66) which on eliminating χ give one equation for ϕ_0.

The complex manner in which ϕ_0 enters into the equation renders solution difficult except by trial, in which way values of ϕ_0 corresponding to different values of c have been found.

The value of ϕ_0 substituted in equations (58) or (66) gives χ and ϕ_1.

The corresponding values of c_1, ϕ_0 and χ being thus obtained, a complete table might be calculated. This, however, has not been done, as there does not exist sufficient experimental data to render such a table necessary.

What has been done is to obtain ϕ_1 and ϕ_0 for $c = \cdot 5$, θ_1 having the value 1·3704 as in equation (88) and in TOWER's experiments.

The value $c = \cdot 5$ was chosen by a process of trial in order to correspond with the experiments in which Mr. TOWER measured the pressure at different parts of the journal as described in his second report, and as being the greatest value of c for which complete lubrication is certain.

Putting $c = \cdot 5$, equations (43) and (44) give

$$\left.\begin{array}{ll} A_0=-1{\cdot}5351-2{\cdot}3018\chi & B_0=-\ {\cdot}012-2{\cdot}304\chi \\ A_1=\ \ 3{\cdot}0723+3{\cdot}0721\chi & B_1=\ \ 2{\cdot}143+2{\cdot}286\chi \\ A_2=\ \ 1{\cdot}8647+1{\cdot}5360\chi & B_2=\ \ 1{\cdot}139+\ {\cdot}896\chi \\ A_3=-\ {\cdot}8911-\ {\cdot}6571\chi & B_3=-\ {\cdot}455-\ {\cdot}316\chi \\ A_4=-\ {\cdot}3753-\ {\cdot}2582\chi & B_4=-\ {\cdot}146-\ {\cdot}097\chi \\ A_5=\ \ {\cdot}1396+\ {\cdot}1343\chi & \end{array}\right\} \quad . \ . \ . \ . \quad (99)$$

Taking

$$\theta_1=1{\cdot}3704 \quad \text{or} \quad 78^\circ\ 31'\ 30''$$

it was found by trial that when . . . . (100)

$$\phi_0=48^\circ$$

and K_2 was neglected (under the circumstances K_2 was about ·0003K_1), equation (58) gave

$$\chi=-{\cdot}82295 \quad \text{or} \quad -\sin 55^\circ\ 22'\ 40''$$

and equation (66) gave . . . . (101)

$$\chi=-{\cdot}82274 \quad ,, \quad -\sin 55^\circ\ 21'\ 40''$$

The difference ·00021 being in the same direction and about the magnitude of the effect of neglecting K_2.

This solution was therefore sufficiently accurate, and adopting the value of $\phi_1-\phi_0$

$$\phi_1=7^\circ\ 21'\ 40'' \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (102)$$

Equations (99) then became

$$\left.\begin{array}{ll} A_0=\ \ {\cdot}3587 & B_0=\ 1{\cdot}912 \\ A_1=\ \ {\cdot}5449 & B_1=\ 2{\cdot}263 \\ A_2=\ \ {\cdot}6010 & B_2=\ \ {\cdot}303 \\ A_3=-{\cdot}3505 & B_3=-\ {\cdot}195 \\ A_4=-{\cdot}0407 & B_4=\ \ {\cdot}066 \\ A_5=-{\cdot}0291 & \end{array}\right\} \quad . \ . \ . \ . \ . \ . \ . \quad (103)$$

Substituting the values from equations (100), (102), and (103) in

equation (67)

$$\frac{L}{R}=-1{\cdot}2752K_1c \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (104)$$

equation (68)

$$\frac{M}{R^2}=-4{\cdot}7546K_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (105)$$

By equation (59)

$$E=-{\cdot}25257 \quad \ldots \ldots \quad (106)$$

By equation (60)

$$\begin{aligned}\frac{p-p_0}{K_1c}=&-{\cdot}25257+{\cdot}3587\theta-{\cdot}545\cos(\theta-48^\circ)\\&+{\cdot}3005\sin 2(\theta-48^\circ)+{\cdot}1168\cos 3(\theta-48^\circ)\\&-{\cdot}0407\sin 4(\theta-48^\circ)+{\cdot}0058\cos 5(\theta-48^\circ)\end{aligned} \quad \ldots \ldots \quad (107)$$

From equation (107) values of

$$\frac{p-p_0}{Kc}$$

have been found for values of θ differing by 10°, and at certain particular values of θ—

$$\left.\begin{array}{ll}\theta=\pm 29^\circ\ 20'\ 20'' & \text{points at which the pressure was measured}\\ \theta=-\ 7^\circ\ 21'\ 40'' & \text{point of maximum pressure}\\ \theta=-76^\circ\ 38'\ 40'' & \text{point of minimum pressure}\\ \theta=\pm 78^\circ\ 31'\ 30'' & \text{the extremities of the brass}\end{array}\right\} \quad . \quad (108)$$

These are given in Table II.

TABLE II.—The pressure at various points round the bearing.

θ off side.	Arc radius = 1.	$\frac{p-p_0}{-K_1c}$.	θ on side.	Arc radius = 1.	$\frac{p-p_0}{-K_1c}$.
0° 0′ 0″	0·0	1·0151	0° 0′ 0″		1·0151
− 7 21 40	−0·12837	1·0269			
−10 0 0	−0·17453	1·0232	10 0 . 0	0·17453	0·9331
−20 0 0	−0·34907	0·9412	20 0 0	0·34907	0·8022
−29 20 20	−0·5120	0·7923	29 20 20	0·5120	0·6609
−40 0 0	−0·6981	0·5612	40 0 0	0·6981	0·5003
−50 0 0	−0·8737	0·3349	50 0 0	0·8737	0·3555
−60 0 0	−1·0472	0·1449	60 0 0	1·0472	0·2249
−70 0 0	−1·2217	0·0293	70 0 0	1·2217	0·1002
−76 38 20	−1·3367	−0·001			
−78 31 20	−1·3704	0·0002	78 31 20	1·3704	0·0002

The figs. 2, 3, 4 (Plate 8) represent the results of Table II.

In the curve figure (2) the ordinates are the pressures, and the abscissæ the arcs corresponding to θ.

In the curve figure (3) the ordinates are the same plotted to abscissæ$=R\sin\theta$.

In the curve figure (4) the horizontal ordinates are the same as the vertical ordinates in figs. 2 and 2, and the vertical abscissæ are$=R\cos\theta$.

These theoretical results will be further discussed in Section IX., where they will be compared with Mr. TOWER'S experiments.

29A. $c=\cdot 5$ *is the limit to this Method of Integrating.*

In the case considered, in which $\theta=78^\circ\ 31'\ 20''$, Table II., shows that the pressure towards the extreme off side is just becoming negative. With greater values of c this negative pressure would increase according to the theory.

The possibility of this negative pressure would depend on whether or not the extreme off edge of the brass was completely drowned in the oil bath, a condition not generally fulfilled, and even then it is doubtful to what extent the negative pressure would hold, probably not with certainty below that of the atmosphere.

With an arc of contact anything like that of the case considered it would be necessary, in order to proceed to larger values of c than 5, that the limits between which the equations have been integrated would have to be changed from

$$-\theta_1,\ +\theta_1,$$

to

$$2\left(\phi_0-\frac{\pi}{2}\right)-\phi_1,\ +\theta_1.$$

This integration has not been attempted, partly because it only applies, in the case of complete lubrication, when the value of $c.>\cdot 5$ renders approximation very laborious, but chiefly because it appears almost obvious that the value of c, which renders the pressure negative at the off extremity of the brass is the largest value of c under which lubrication can be considered certain.

The journal may run with considerably higher values of c, the continuity of the film being maintained by the pressure of the atmosphere, which would be most likely to be the case with high speeds. But although the load which makes $c=\cdot 5$ is not necessarily the limit of carrying power of the journal, it would seem to be the limit of the safe working load, a conclusion which, as will appear on considering Mr. TOWER'S experiments, seems to be in accordance with experience.

This concludes the hydro-mechanical theory of lubrication so far as it has been carried in this investigation. There remain, however, physical considerations as to the effect of variations of the speed and load on a and μ which have to be taken into account before applying the theory.

SECTION VIII.—THE EFFECTS OF HEAT AND ELASTICITY.

30.—μ *and* a *are only to be inferred from the experiments.*

The equations of the last section give directly the friction, the intensity of pressure, and the distance between the cylindrical surfaces, when the velocity, the radii of curvature of the journal and the brass, the length of the brass, and the manner of loading are known (*i.e.*, when U, R, a, θ_1, L, and μ are known); and, further, if M the moment of friction is known, the equations afford the means of determining a when μ is known, or μ when a is known.

The quantities U, R, θ_1, and L are of a nature to be easily determined in any experiment or actual case, and M is easily measured in special experiments, but with a and μ it is different.

By no known means can the difference of radii (a) of the journal and its brass be determined to one ten-thousandth part of an inch, and this would be necessary in order to obtain a precise value of a. As a matter of fact even a rough measurement of a is impossible. To determine a, therefore, it is necessary to know the moment of friction or the distribution of pressure; then if the value of μ be known by experiments such as those described for olive oil (Section II.), a can be deduced from the equations for any particular value of μ. But although the values of μ may have been determined for all temperatures for the particular oil used, and that value chosen which corresponds with the temperature of the oil bath in the experiment, the question still arises whether the oil bath (or wherever the temperature is measured) is at the same temperature as the oil film. Considering the thinness of the film and the rapid conduction of heat by metal surfaces, it seemed at first sight reasonable to assume that there would be no great difference, but when on applying the equations to determine the value of a for one of the journals and brasses used in Mr. TOWER's experiments, it was found that the different experiments did not give the same values for a, and that the calculated values of a increased much faster with the velocity when the load was constant than with the load when the velocity was constant, it seemed probable that the temperature of the oil film must have varied in a manner unperceived, increasing with the velocity and diminishing the viscosity, which would account for an apparent increase of a.

That a should increase with the load was to be expected, considering that the material of both journal and brass are elastic, and that the loads range up to as much as 600 lbs. per square inch, but there does not appear any reason why a should increase with the velocity unless there is an increase of temperature in the metal. If this occurs, the apparent increase of a would be part real and part due to the unappreciated diminution of μ owing to the rise of temperature.

Until some law of this variation of temperature and of the variation of a with the load is found, the results obtained from the equations, with values of μ corresponding to some measured temperature, such as that of the oil bath or a point in the brass, can only be considered as approximately applicable to actual results. Even so, however, the degree of approximation is not very wide as long as the conditions are such that the journal "runs cool."

But, treated so, the equations fail to show in a satisfactory way what is one of the most important matters connected with lubrication—the circumstances which limit the load which a journal will carry. For, although it may be assumed that the limit is reached when ca, the shortest distance between the surfaces, becomes zero or less than a certain value, yet, according to the equations, assuming a and μ to be constant, the value of c increases directly as U if the load be constant; so that the limiting load should increase with U. But this is not the case, for it seems from experiments that at a certain value of U the limiting load is a maximum if it does not diminish for a further increase of U.

Although, therefore, the close agreement of the calculated distribution of the pressure over the bearing with that observed and the approximate agreement of the calculated values of the friction for different speeds and loads, such as result when μ and a are considered constant, seem to afford sufficient verification of the theory, and hence a sufficient insight into the general action of lubrication, without entering into the difficult and somewhat conjectural subject of the effects of heat and elasticity, yet the possibility of obtaining definite evidence as to the circumstances which determine the limits to lubrication, which, not having been experimentally discovered, are a great desideratum in practice, seemed to render it worth while making an attempt to find the laws connecting the velocity and load with a and μ.

As neither the temperature of the oil film or the interval between the surfaces can be measured, the only plan is to infer the law of the variations of these quantities from such complete series of experiments as Mr. TOWER's. In attempting this, a probable formula with arbitrary constants is first assumed or deduced from theoretical considerations, and then these constants are determined from the experiment and the general agreement tested. In order to determine the actual circumstances on which the constants depend, it is important to obtain the formula from theoretical considerations. This has therefore been done, although these considerations would not be sufficient to establish the formulæ without a close agreement with the experiments.

31. *The Effect of the Load and Velocity to alter the Value of the Difference of Radii of the Brass and Journal,* i.e., *of a.*

The effect of the load is owing to the elasticity of the materials, hence it is probable that the effect will be proportional to the load L. To express this put—

$$a=a_0+m\text{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (109)$$

The effect of the temperature on a is owing to the different coefficients of expansion of brass and iron. Thus :—

$$a_T - a_0 = (B' - S')\,(T - T_0)R,$$

where B' and S' are the respective coefficients of expansion of the bearing and journal. These for brass and iron are :—

$$B' = \cdot 0000111$$
$$S' = \cdot 0000061,$$

therefore putting $T - T_0 = Tm$ (the mean rise of temperature due to friction)

$$a_T = a_0\left(1 + \cdot 000005\frac{R}{a_0}Tm\right)$$
$$= a_0(1 + ETm) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (110)$$

Putting

$$E \text{ for } \cdot 000005\frac{R}{a_0}$$

If, as seems general, a_0 is about ·0005 inch, then with a 4-inch journal

$$E = \cdot 02 \text{ about} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (111)$$

which is sufficiently large to be important.

32. *The Effect of Speed on the Temperature.*

Putting—

T_0 the temperature of the surroundings and bath.
T_1 the mean temperature of the oil as it is carried out of the film.
T_m the mean rise in temperature of the film due to friction.
Q the volume of the oil carried through per second.
D the density.
S the specific heat.
H the heat generated.
H_1 the heat lost by conduction.
C' a coefficient of conduction.

taking the inch, lb. and degree Fahr. as units, and 12 J as mechanical equivalent of heat.

$$Q = \frac{Uh_1}{2}$$

$$H = \frac{2R\theta f U}{12J}$$

$$H_1 = 2R\theta C'T_m$$

$$T_1 - T_0 = \frac{H - H_0}{DSQ}.$$

Putting

$$H-H_1=qT_mQ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (112)$$

where q is a constant depending on the relative values of $T-T_0$ and T_m, also on how far the metal of the journal assists the oil in carrying out heat.

On substituting the values of H_1, H_2, Q, it appears

$$T_m=\frac{fU}{\frac{3JDSqh_1U}{R\theta}+B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (112\text{A})$$

$$B=12JC'$$

There does not appear to be any reason to assume any of the quantities in the denominator to be functions of the temperature except h_1. By equation (42)

$$h_1=a\{1+c\sin(\phi_1-\phi_0)\}$$

Equation (112A) may thus have the form

$$T_m=\frac{f}{A(1+ET_m)+\frac{B}{U}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (113)$$

Where

$$A=3JDSqa_0(1+ml)\{1+c\sin(\phi_1-\phi_0)\} \quad . \quad . \quad . \quad . \quad (114)$$

This shows that A is a function of the load, increasing as the first power and diminishing as the second power, but the experiment show the effects of these terms are small, and A is constant except for extreme loads.

33. *The Formulæ for Temperature and Friction, and the Interpretation of the Constants.*

From equation (8), Section II.

$$\left.\begin{array}{l}\mu=\mu_0{}^{-C(T-T_0)} \\ C=0221 \text{ (for olive oil)}\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115)$$

From equations (109) and (110)

$$a=(a_0+ml)\{1+E(T-T_0)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (116)$$

or approximately since $E(T_1-T_0)$ is small

$$a=(a_0+ml)e^{E(T-T_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (117)$$

Whence substituting in the equation which results from (51) c being small

$$f=\frac{\mu}{a}\mathrm{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (118)$$

Putting T_x for any particular temperature μ_x a_x corresponding values

$$f=\frac{\mu_x}{a_x+ml}\mathrm{U}e^{-\{\mathrm{C}+\mathrm{E}\}(\mathrm{T}-\mathrm{T}_x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (119)$$

From (113)

$$f=\mathrm{A}\{\mathrm{T}_m+\mathrm{E}\mathrm{T}^2_m\}+\frac{\mathrm{B}}{\mathrm{U}}\mathrm{T}_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (120)$$

These equations (119) and (120) are independent, and therefore furnish a check upon each other when the constants are known.

Thus substituting the experimental values of U and f in (120) a series of values of T_m are obtained, which when substituted in (119) should give the same value of f.

In these equations the meaning of the constants is as follows :—

C is the rate at which viscosity increases with temperature.

E is the rate at which a increases with temperature, owing to the different expansion of brass and iron.

AU expresses generally the mechanical equivalent of the heat which is carried out of the oil film by the motion of the oil and journal for each degree rise of temperature in the film.

B expresses the mechanical equivalent of the heat conducted away through the brass and journal.

The respective importance of these two coefficients is easily apparent. When the velocities are low but little heat will be carried out, and hence the temperature of the journal depends solely on the value of B. But when the velocities are high, B becomes insignificant compared with AU, and it is A alone which keeps the journal cool.

The value of A may to some extent be inferred from the quantities which enter into it as in equation (114). Thus in the case of Mr. TOWER's experiment, since

$\mathrm{R}=2$ $\quad\theta=1{\cdot}37$ $\quad a={\cdot}00075$ $\quad\mathrm{J}={\cdot}772$
$\mathrm{D}=0{\cdot}033$ $\quad\mathrm{S}=0{\cdot}31$ (for olive oil)

$$\mathrm{A}={\cdot}0063q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (121)$$

It is very difficult to form an estimate of q, but it would seem probable that it has a value not far from 2 ; and, as will be subsequently shown, in the case of Mr. TOWER's experiments, q is about 3·5 or

$$\mathrm{A}=0{\cdot}0223 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (122)$$

As B expresses the rate at which the heat generated in the oil film is carried away by conduction through the oil and the surrounding metal, any estimate of its value is very difficult. If we could measure the temperature at the surfaces of the metal, B might be made to depend only on the thickness and conductivity of the oil film. But before heat can escape from the journal or bearing it must pass along intricate metal channels formed by the journal or shaft and its supports ; and, on consideration, it appears that in ordinary cases the resistance of such channels would be much greater than the resistance of the oil film itself. For example, in the case of a railway axle, the heat generated must escape either along the journal to the nearest wheel or through the brass and the cast-iron axle box to the outside surface, so that either way it must traverse at least three or four inches of iron. This is about the best arranged class of journals for cooling. In most other cases heat has much further to go before it can escape. However, in every case B will depend on the surrounding conditions and can only be determined by experiment. From the experiments, to be considered in the next section, it appears that

$$B=1 \text{ (about)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (123)$$

But it is to be noticed that Mr. TOWER has introduced a somewhat abnormal condition by heating the oil bath above the surrounding temperature. For in this way, letting alone the heat generated by friction, there must have been a continual flow of heat from the bath along the journal to the machinery ; and, considering the comparatively limited surface of the journal in contact with the hot oil and the large area of section of the journal, it appears unlikely that the temperature of the journal was raised by the bath to anything like the full temperature of the latter, a conclusion which is borne out by Mr. TOWER's experiments with different temperatures in the bath (Table XII., Art. 34), which shows that the temperature of the bath produced a much smaller effect on the friction than would have followed from the known viscosity of oil had the temperature of the oil film corresponded with the temperature of the bath.

Thus the temperature of the film independent of friction is not the temperature of the bath or surrounding objects, and as it is unknown until determined from the experiments, it will be designated as

$$T_x,$$

and the suffix x used to designate the particular value for $T=T_x$ of all those quantities which depend on the temperature as

$$\mu_x \quad a_x$$

If T be the mean temperature of the film,

$$T-T_x=T_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (123\text{A})$$

where T_m is the rise of temperature due to the film.

33A. *The maximum Load the Journal will carry at any Speed.*

It has already been pointed out that the carrying power of the journal is at its greatest when c is between ·5 and ·6. If, therefore, taking the load constant, c passes through a minimum value as the velocity increases with a constant load, then the load which brings c to a constant value will be a maximum for some particular velocity, and if the particular value of c be that at which the carrying power is greatest, the carrying power will be greatest at that particular speed.

The question whether, according to the theory, journals have a maximum carrying power at any particular speed turns on whether

$$\frac{d\mathrm{L}}{d\mathrm{U}}\,(c \text{ being constant})$$

is zero for any value of U.

This admits of an answer if the values for μ, a, T_x, and equations (119) and (120) hold, for when c is constant $\frac{\mathrm{L}}{\mathrm{K}_1\mathrm{U}}$, $\frac{f}{\mathrm{K}_2\mathrm{U}}$, and A are constant, whence differentiating and substituting it appears that when c is constant

$$\frac{d\mathrm{L}}{d\mathrm{U}}=\frac{\mathrm{L}}{\mathrm{U}}\,\frac{\mathrm{A}+\frac{\mathrm{B}}{\mathrm{U}}+\left(\mathrm{AE}-(3\mathrm{E}+\mathrm{C})\frac{\mathrm{B}}{\mathrm{U}}\right)\mathrm{T}-\mathrm{AE}^2\mathrm{T}^2}{\mathrm{A}+\frac{\mathrm{B}}{\mathrm{U}}+\left\{(3\mathrm{E}+\mathrm{C})\mathrm{A}+(\mathrm{E}+\mathrm{C})\frac{\mathrm{B}}{\mathrm{U}}\right\}\mathrm{T}+\mathrm{AE}(\mathrm{E}+\mathrm{C})\mathrm{T}^2} \quad . \quad . \quad . \quad . \quad (123\text{B})$$

where U is to be taken positive, and T increases as U increases. This shows that $\frac{d\mathrm{L}}{d\mathrm{U}}$, for a constant value of c, changes sign for some value of U if T continues to increase with U.

Hence, according to the theory, the values of L, which make c constant as U increases, approach a maximum value as U increases, and since this value, when c is about ·5, represents the carrying power of the journal, this approaches a maximum as U increases.

Section IX.—APPLICATION OF THE EQUATIONS TO MR. TOWER'S EXPERIMENTS.

34. *References to* MR. TOWER'S *Reports.*

From the experiments described in MR. TOWER'S Reports I. and II., in the Minutes of the Institution of Mechanical Engineers, 1884, the journal had a diameter of 4 inches, and the chord of the arc covered by the brass was 3·92 inches, the length of the brass being 6 inches.

The loads on the brass in lbs., divided by 24, are called the *nominal load per square inch.*

The moments of friction in inches and lbs., divided by 24 × R, are called the nominal friction per square inch.

These nominal loads, and nominal frictions, with the number of revolutions from 100 to 450, at which they were taken, are arranged in tables for each kind of oil used, and also for the same oil at different temperatures of the bath.

All the tables relative to the oil bath in the first report refer to the same brass and journal. And with this brass, to be here called No. 1, no definite measurements of the actual pressure were made.

The second report contains the account of the pressure measurements, but it is to be noticed that these were made with a new brass, here called No. 2, and that the only friction measurements recorded with this brass are three made at velocities five times less than the smallest velocity used in the case of brass No. 1.

It thus happens that while by the application of the foregoing theory to the friction experiments on brass No. 1 a value is obtained for *a*, the difference in radii of brass No. 1 and the journal; and from the pressure experiments on brass No. 2 a value is obtained for *a* in the case of brass No. 2; since these are different brasses there is no means of checking the one estimate against the other.

The following tables extracted from Mr. TOWER's reports are those to which reference has chiefly to be made.

The first of these extracts is a portion of Table I, in Mr. TOWER's first report; this related to olive oil, but corresponds very closely with the results for lard oil also, although not quite so close for mineral oil.

The second extract is Table IX. in the first report; this shows the effect of temperature on the friction of the journal with lard oil.

The third extract is from the second report, being Table XII., representing the oil pressure at different parts of the bearing as measured with brass No. 2.

FROM Table I. (Mr. TOWER's 1st Report, Brass No. 1.) Bath of Olive Oil. Temperature, 90 deg. Fahr., 4-in. journal, 6-in. long, Chord of arc of contact=3·92 in.

Nominal load lbs. per square inch. Total load divided by 4 × 6.	Nominal friction per square inch of bearing.							
	100 rev. 105 ft. per min.	150 rev. 157 ft. per min.	200 rev. 209 ft. per min.	250 rev. 262 ft. per min.	300 rev. 314 ft. per min.	350 rev. 360 ft, per min.	400 rev. 419 ft. per min.	450 rev. 471 ft. per min.
520	..	·416	·520	·624	·675	·728	·779	·883
468	..	·514	·607	·654	·701	·794	·841	·935
415	..	·498	·580	·622	·705	·787	·870	·995
363	..	·472	·580	·616	·689	·725	·798	·907
310	..	·464	·526	·588	·650	·680	·742	·835
258	·361	·438	·515	·592	·644	·669	·747	·798
205	·368	·43	·512	·572	·613	·675	·736	·818
153	·351	·458	·535	·611	·672	·718	·764	·871
100	·36	·45	·555	·63	·69	·77	·82	·89

FROM MR. TOWER'S 1st Report, Brass No. 1.

TABLE IX. Bath of Lard Oil. Variation of Friction with Temperature. Nominal Load 100 lbs. per square inch.

Temperature. Fahr.	Nominal friction per square inch of bearing.							
	100 rev. per min.	150 rev. per min.	200 rev. per min.	250 rev. per min.	300 rev. per min.	350 rev. per min.	400 rev. per min.	450 rev. per min.
° 120	·24	·29	·35	·40	·44	·47	·51	·54
110	·26	·32	·39	·44	·50	·55	·59	·64
100	·29	·37	·45	·51	·58	·65	·71	·77
90	·34	·43	·52	·60	·69	·77	·85	·93
80	·4	·52	·63	·73	·83	·93	1·02	1·12
70	·48	·65	·8	·92	1·03	1·15	1·24	1·33
60	·59	·84	1·03	1·19	1·30	1·4	1·48	1·56

FROM MR. TOWER'S Second Report, Brass No. 2. Heavy Mineral Oil. Nominal Load 333 lbs. per square inch. Number of revolutions 150 per minute. Temperature, 90°.

TABLE XII. Oil pressure at differents points of a bearing.

Longitudinal planes	on	centre	off
Pressure per square inch	lb.	lb.	lb.
Transverse plane, middle	370	625	500
Transverse plane, No. 1	355	615	485
Transverse plane, No. 2	310	565	430

The points at which the pressure was measured were at the intersections of six planes, three parallel vertical longitudinal planes parallel to the axis of the journal, one through the axis, and the other two, one on the *on* and the other on the *off* side, both of them at a distance of ·975 inch from that through the axis, three transverse planes, one in the middle of the journal, the other two respectively at a distance of one and two inches on the same side of that through the middle.

In referring to these experimental results in the subsequent articles,

The nominal load per square inch is expressed by L′;

The number of revolutions per minute by N′;

The nominal friction by f';

The effect of the fall of pressure at the ends of the journal on the mean pressure is expressed by $\frac{1}{s}$, thus—

n is a coefficient depending on the way in which the journal fits the shaft.

$$\left.\begin{aligned} L' &= \frac{L}{4s} \\ f' &= \frac{nM}{4R} \\ N' &= -\frac{U \times 60}{2\pi R} \\ s &= 1{\cdot}21 \end{aligned}\right\} \quad \dots \quad (124)$$

35. *The Effect of Necking the Journal.*

The expression (124) for f' assumes that the journal was not necked into the shaft. From Mr. TOWER'S reports it does not appear whether or not the brass was fitted into a neck on the shaft; but since there is no mention of such necking, the theory is applied on the supposition that there was not.

If there were, the friction at the ends of the brass would increase the moment of friction. Put b for the depth of the neck and a' for the thickness of the oil film at the ends, then the moment of resistance of these ends would be—

$$\frac{\mu}{a'} \times \frac{N\pi}{30}\left(R+\frac{b}{2}\right)^3 b.$$

Hence if M be the moment of friction of the cylindrical portion of the journal only

$$24f' - 2\frac{\mu}{a}\,\frac{\pi N}{30}\,6\left(R+\frac{b}{2}\right)^3 = 6\frac{M}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (125)$$

And from equation (97)—

$$f' = \frac{\pi N}{360}\,\frac{\mu}{a}\left\{\frac{ab\left(R+\frac{b}{2}\right)^3}{a'R} + 8{\cdot}25R^2\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (126)$$

For example, a 5-inch shaft necked down to a 4-inch journal would give $b = {\cdot}5$ inch. Whence, assuming

$$\text{and} \qquad \left.\begin{aligned} a' &= {\cdot}0005 \\ \frac{a}{a'} &= 2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (127)$$

the relative friction of the ends to that of the journal would be 11·36 to 31·00, or

28 per cent. of the friction; and the values of a, calculated on the assumption of no necking, would have to be increased in the ratio $n=1{\cdot}33$.

Even if there is no necking the value of a will probably not be the same all along the journal, in which case the values of a^2 and a in K_1 and K_2 will be means, and then the square of the mean will be less than the mean of the squares, so that n will probably have a value greater than unity, although there may be no necking of the shaft.

36. *A first Approximation to the Difference in the Radii of the Journal and Brass No.* 1.

The recorded temperature in Mr. TOWER's Table I. is 90° Fahr. Accepting this, and taking the value of μ, equation (8), Section II.,

$$\mu_{90}=10^{-6}\times 6{\cdot}81 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (128)$$

By equation (97)—

$$\frac{n\mu}{a}=\frac{-nM}{2{\cdot}75R^2U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

Since $R=2$ and $U=-\frac{4\pi N}{60}$

$$\frac{n\mu}{a}=-\frac{72f'}{U}$$

$$=3{\cdot}46\frac{f'}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (130)$$

Whence substituting from equation (128) for μ_{90}

$$\frac{a}{n}=10^{-6}\times 1{\cdot}97\frac{N}{f'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (131)$$

and from the tabular Nos. for $L'=100$,

$$\left.\begin{array}{l} N=100, \quad f'={\cdot}36 \\ \frac{a}{n}=10^{-4}\times 5{\cdot}5 \text{ (inch)} \\ N=480, \quad f'={\cdot}89 \\ \frac{a}{n}=10^{-4}\times 10 \text{ (inch)} \end{array}\right\} \quad . \quad . \quad . \quad . \quad (132)$$

These are the extreme cases; for intermediate velocities intermediate values of $\frac{a}{n}$ are found.

In order to be sure that these are the values of $\frac{a}{n}$, which result from the application of the equations, it is necessary (since the approximate equations only have been used) to see that the squares of c may be neglected.

Substituting from equation (124) in (96)

$$c = \cdot 338 na \frac{L's}{f'R}$$

which for $L'=100$, $N=100$, gives

$$c = \cdot 033 n^2 \qquad \qquad (133)$$

and for $L'=100$, $N=450$,

$$c = \cdot 065 n^2$$

So that the approximations hold, and, as already stated in Art. 30, this considerable increase in the value of a with the load constant suggests that the temperature of the film was not really 90°. And as this point has been considered in the last section the equations of that section may be at once used to determine the law of this temperature, after which the values of $\frac{a}{n}$ may be determined with precision.

37. *The Rise in Temperature of the Film owing to Friction.*

In order to determine the values of E, A, and B in equations (119) and (120), by substituting in these equations corresponding values of N and f' for $L'=100$, the tabular values of f' were somewhat rectified by plotting and drawing the curve N, f'. These corrected values are in the second row, Table III.

From these values, and the corresponding values of N, it was then found by trial that the equations (119) and (120) respectively

$$f = \frac{\mu_x}{a_x + mL_s} U e^{-(C+E)(T-T_x)}$$

$$f \doteq A\{T_m + ET_m{}^2\} + \frac{B}{U}(T_m)$$

$$c = \cdot 0221$$

are approximately satisfied for values of $T - T_x = T_m$, if

$$\frac{\mu_x}{a_x + m \times 400} = \frac{\cdot 01345}{n} \qquad \qquad (134)$$

$$\left.\begin{aligned} A &= \cdot 022308 \\ E &= \cdot 0222 \\ B &= \cdot 95914 \end{aligned}\right\} \qquad \qquad (135)$$

Which seemed to agree very well with the reasoning Section VIII. With these values of the constants the values of $T-T_x$ were then calculated from equation (120), and are given in the third row in Table III. These temperatures were then substituted in equation (119), and the corresponding values of f calculated, these are given in the fourth row, Table III.

TABLE III.—Rise of Temperature in the Film of Oil caused by Friction, calculated by Equation (120) from Experiments with a Nominal Load 100 lbs. (see Table I., TOWER, Art. 34).

Nominal friction per square inch, as calculated by equation (119) from the rise of temperature.										
Nominal load per square inch $L'=100$ lbs.	N	Revolutions per minute	100	150	200	250	300	350	400	450
	f	Nominal friction per square inch for olive oil: Table I., TOWER	·36	·45	·54	·63	·69	·77	·82	·89
		Nominal friction per square inch for olive oil: Corrected to a curve . . .	·33	·55	·55	·63	·705	·758	·83	·89
	$T-T_0$ Fahr.	Rise of temperature by equation (120)	3·45	5·83	8·13	10·02	11·77	13·26	14·48	15·37
	f_1	Nominal friction per square inch calculated by equation (119) assuming c small	·336	·453	·546	·628	·697	·76	·823	·89

The agreement between these calculated values of f and the experimental values is very close; and it may be noticed that a very small variation in any of A, B and E makes a comparatively large difference in some one or other of the calculated values of f, or, in other words, these are the only positive values of these quantities which satisfy the equations.

The only difference between the experimental and calculated values of f which is not explainable as experimental error, is for the lowest speed at which the experimental value of f is 6·7 per cent. too large. This is important as it is in accordance with what might be the result of neglecting c^2, since at that speed c is becoming too large to be neglected, and taking c^2 into account the calculated value of f agrees very closely with the experimental.

38. *The Actual Temperature of the Film.*

Having found the approximate values of T_m, the rise of temperature, owing to friction, it remains to find T_x, the temperature of the film, the rise due to friction, so that

$$T_x+T_m=\text{temperature of film.}$$

This is found from Mr. TOWER's Table XI. (see Art. 34).

Putting

T_B for temperature of the bath
T_0 for temperature of surrounding objects

and assuming

$$T_x+T_m=Z(T_B-T_0)+T_m+T_0 \qquad (136)$$

From equations (119) and (130)

$$f = \frac{\text{N}}{3{\cdot}46} \cdot \frac{n\mu_0}{a_0 + m\text{L}} e^{-{\cdot}0443\{\text{Z}(\text{T}_\text{B} - \text{T}_0) + \text{T}_m\}}$$

whence

$$\log f = -{\cdot}0443\{\text{Z}(\text{T}_\text{B} - \text{T}_0) + \text{T}_m\} \log e + \log\left(\frac{\text{N}}{3{\cdot}46} \frac{\mu_0}{a_0 + m\text{L}}\right) \quad . \quad . \quad (137)$$

In Table IX. (Tower) the values of f are given for the same values of N′ and L′ corresponding to different values of T_B.

Substituting corresponding values of f and T_B in equation (137), and subtracting the resulting equations, we have an equation in which the only unknown quantities are Z and the differences of T_m.

The values of f' being known, the values of T_m are obtained from equations (120), (134), and (125), and substituting these, the equations resulting from (137) give the values of Z. Thus from Table IX. (Tower)

$$\text{L}' = 100$$
$$\text{U} = 100$$

$$\text{T}_\text{B} = 60 \qquad f = {\cdot}59 \qquad \text{T}_m = 5{\cdot}9$$
$$\text{T}_\text{B} = 70 \qquad f = {\cdot}48 \qquad \text{T}_m = 4{\cdot}8$$

From (137)

$$\text{Z} + \frac{5{\cdot}9 - 4{\cdot}8}{10} = \frac{\log {\cdot}59 - \log {\cdot}48}{{\cdot}0443 \times 10 \times \log e}$$

Therefore

$$\text{Z} = 35 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (138)$$

From this value of Z the values of f' corresponding to those in Tower's Table IX. have been calculated and agree well with the experimental values.

The smallest temperature of the oil bath recorded in Tower's Table IX. is 60° Fahr., therefore it is assumed that this was the normal temperature, whence

$$\text{T}_x = {\cdot}35(\text{T}_\text{B} - 60) + 60 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (139)$$

Hence it is concluded that the actual temperature of the oil film in all the experiments with the bath, at a temperature of 90° Fahr., is given by

$$\text{T} = 70{\cdot}5 + \text{T}_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (140)$$

By the formula for μ since $\text{T}_x = 70{\cdot}5$

$$\begin{aligned} \mu_x &= {\cdot}00004737 e^{-{\cdot}0021 \times 70{\cdot}5} \\ &= {\cdot}000009974 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (141) \\ &= {\cdot}00001 \text{ (approximately)} \end{aligned}$$

and since, by equation (134), when $L'=100$

$$
\begin{aligned}
a_x &= \frac{n\mu_x}{\cdot 01345} \\
&= \cdot 0007413n \qquad \qquad (142) \\
&= \cdot 00074n \text{ (approximately).}
\end{aligned}
$$

This is the value of a_x with a load of 100 lbs. per square inch.

39. *The Variation of a with the Load.*

All Mr. TOWER's experiments, when the loads are moderate and the velocities high, show a diminution of resistance with an increased load.

Since c increases with the load and the friction increases as c increases, a and μ being constant, the diminution of friction with increased loads shows either that the load increases the temperature of the film and so diminishes the viscosity, or increases the radius of curvature of the brass as compared with that of the journal, *i.e.*, increases a.

These effects have been investigated by substituting the experimental values of f' and L', obtained with the same velocity in equations (119) and (120).

In this way, from equation (119) the value of m is determined, where, from equations (117) and (135),

$$a_x=(a_0+mL')ne^{\cdot 0222(T_x-T_0)} \qquad \qquad (143)$$

And the equation (120) gives the effects of the load on the value of the constant A. After trial, however, it appears that the effects of the load upon the constant A are small so long as the loads are moderate, and that the diminution of the resistance with the increased load is explained by the value obtained for m from equation (119). From this equation, taking $L'_1\ f'^1$, $L'_2\ f'^2$, simultaneous values of L' and f', and assuming T_x independent of the load

$$\frac{a_0+mL'_1}{a_0+mL'_2}=\frac{f'^2}{f'^1} \qquad \qquad (144)$$

which gives the value of m.

The slight irregularities in the experiments affect the values of m thus found to a considerable extent, and a mean has been taken, which is

$$m=\cdot 002a_0 \qquad \qquad (145)$$

Putting $T_x=70\cdot 5$, $T_0=60$, $a_x=\cdot 00074$, when $L'=100$, from equation (143)

$$a_0+mL'=\cdot 0005861n.$$

Therefore

$$a_0=\cdot 0004885n \qquad \qquad (146)$$

The value for a thus obtained is therefore

$$a = \cdot 0004885 n (1 + \cdot 002\,\mathrm{L}') e^{\cdot 0222(\mathrm{T}_s + \mathrm{T}_m - \mathrm{T}_0)} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (147)$$

and for the experiments with the bath at 90° Fahr.

$$a = \cdot 0004885 n (1 + \cdot 002\,\mathrm{L}') e^{\cdot 0222(\mathrm{T}_m + 10\cdot 5)}$$

or

$$a = \cdot 0006161 n (1 + \cdot 002\,\mathrm{L}') e^{\cdot 0222\mathrm{T}_m} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (148)$$

From equation (148) and the values of T_m, Table III., the values of

$$\frac{a}{n}$$

for Mr. Tower's experiments have been calculated.

Putting

$$\mu = \cdot 00001 e^{-\cdot 0221\mathrm{T}_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (149)$$

and, substituting in equations (47) from (148) and (149),

$$\left.\begin{aligned} -\mathrm{K}_1 &= \frac{66\cdot 08\,\mathrm{N} e^{-\cdot 0665\mathrm{T}_m}}{(1 + \cdot 002\,\mathrm{L}')^2 n^2} \\ -\mathrm{K}_2 &= \frac{\cdot 0034\,\mathrm{N} e^{-\cdot 0443\mathrm{T}_m}}{(1 + \cdot 002\,\mathrm{L}') n} \\ \frac{\mathrm{K}_2}{\mathrm{K}_1} &= \cdot 00005139 (1 + \cdot 002\,\mathrm{L}') e^{\cdot 0222\mathrm{T}_m} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (150)$$

for the circumstances of Mr. Tower's experiments, to which the equations of Sections VI. and VII. then become applicable.

40. *Application of the Equations to the Circumstances of* Mr. Tower's *Experiments on Brass No.* 1, *given in Table I., Art.* 34, *to determine* e, ϕ_0, ϕ_1, f' *and* $p - p_0$.

The circumstances are, *the unit of length being the inch*,

$$\left.\begin{array}{l} \mathrm{R} = 2 \text{ (inches)} \\ \theta = 78^\circ\ 31'\ 20'' \\ \dfrac{a_0}{n} = \cdot 0004885, \text{ already deduces, equation (146)} \\ \left.\begin{array}{l} \mathrm{L} = 484\,\mathrm{L}' \\ \mathrm{U} = \cdot 2094 \end{array}\right\} \text{equations (124)} \\ \mathrm{T}_0 = 60, \text{ assumed} \\ \mathrm{T}_s = 70\cdot 5, \text{ equation (140)} \\ \mathrm{T}_m = \text{tabular values, Table III., the increase with load being neglected} \end{array}\right\} \quad . \qquad (151)$$

For a first Approximation as long as c is small.

Equations (94), (89), (91), and (95) are used to determine c, ϕ_1, ϕ, f'_1 for the experiments in Table I. (TOWER), these being made with brass No. 1.

Putting as in equation (124)

$$f' = \frac{nM}{2R^2}$$

equation (94) gives

$$f_1' = -1\cdot37\ K_2 n,$$

and by equation (150)

$$f_1' = \cdot004658 \frac{Ne^{-\cdot0443T_m}}{1+\cdot002\,L'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (152)$$

From equation (152) the values of f' to a first approximation have been calculated, using the values of T_m given in Table III. These are given as f_1' in Table IV.

TABLE IV.—Olive Oil, Brass No. 1.

Length of the journal	6 inches.
Chord of the arc of contact of the brass	3·92 inches.
Radius of the journal.	2 inches.
Temperature of the oil bath	90° Fahr.
" surrounding objects	60° Fahr. (assumed).
Difference in radii of brass and journal at 60°	0·0006 inch (deduced).
Effect of necking or variations in radius to increase friction	1·25.

L'	the nominal load in lbs. per square inch, being the total load divided by 24.
N	the number of revolutions per minute.
f'	the nominal friction in lbs. per square inch from Table I. in Mr. TOWER's first Report (see Art. 34).
(f_1')	the nominal friction calculated by complete approximation for $c=5$ (see Art. 40, equation (159)).
f_2'	the nominal friction calculated to a second approximation, equation (154).
f_1'	the nominal friction calculated to a first approximation, equation (152).
c	the ratio of the distance between the centres of the brass and journal to the difference in the radii, equation (153).
a	the difference in the radii of the brass and journal (see equation (157)).
ϕ_1	the angular distance from the middle of the arc of contact of the point of maximum pressure, equation (91).
$\phi_0 - \frac{\pi}{2}$	the angular distance from the middle of the arc of contact of the point of nearest approach (see equation (89)).
T_m	the rise in temperature of the film of oil owing to the friction, equation (120).

	N.	100	150	200	250	300	350	400	450
	T_m Fahr.	3·45	5·83	8·13	10·02	11·77	13·26	14·46	15·37
$L'=415$	f'	..	·498	·580	·622	·705	·787	·870	·995
	(f_1')	..	..	(·57)	(·65)	..	..	..	f_2' ·108
	f_1'	..	·300	·360	·414	·460	·504	·544	·589
	c	..	·67	·578	·520	·487	·457	·436	·418
	a	·00154	·00162	·0017	·00178	·00182	·00187	·00191	·00194
	ϕ_1	..	..	−7° 0′ 0″	−7° 0′ 0″	..	..	..	..
	$\phi_1 - \frac{\pi}{2}$	..	..	−42° 0′ 0″	−42° 0′ 0″	..	..	..	..
$L'=363$	f'	..	·472	·580	·616	·689	·725	·798	·907
	(f_1')	..	(·498)	..	..	..	..	..	f_2' ·920
	f_1'	·233	·314	·378	·434	·482	·526	·573	·616
	c	..	·520	·462	·408	·380	·357	·340	·312
	a	..	·00151	·00161	·00168	·00171	·00177	·00181	·00183
	ϕ_1	..	−7° 0′ 0″	..	..	..	..	..	..
	$\phi_0 - \frac{\pi}{2}$	..	−42° 0′ 0″	..	..	..	..	..	..

TABLE IV.—Olive Oil, Brass No. 1—continued.

N.		100	150	200	250	300	350	400	450
T = Fahr.		3·45	5·83	8·13	10·02	11·77	13·26	14·46	15·37
L′=310	f'	..	·464	·526	·588	·650	·684	·742	·885
	(f_1')	(·370)	..	..	..	..	f_2' ·765	·805	·845
	f_1	·249	·336	·404	·464	·517	·582	·610	·660
	c	·510	·392	·337	·305	·284	·266	·254	·234
	a	·00138	·00144	·00151	·00158	·00161	·00166	·00172	·00172
	ϕ_1	− 7° 0′ 0″	..	..	..	..	..	..	..
	$\phi_0-\frac{\pi}{2}$	−42° 0′ 0″	..	..	..	..	..	..	..
L′=258	f'	·361	·436	·514	·592	·644	·669	·747	·789
	f_2'	..	..	..	·62	·670	·712	·760	·810
	f_1'	·266	·358	·431	·495	·550	·600	·650	·707
	c	·377	·257	·242	·224	·200	·195	·180	·171.
	a	·00128	·00135	·00141	·00148	·00151	·00156	·00159	·00161
	ϕ_1	..	..	..	..	..	..	..	..
	$\phi_0-\frac{\pi}{2}$	..	..	..	..	..	..	..	..
L′=205	f'	·368	·430	·512	·572	·613	·675	·736	·818
	f_2'	·380	·457	·530	·595	·65	·701	·755	·810
	f_1'	·285	·385	·464	·584	·592	·646	·700	·755
	c	·255	·195	·165	·152	·141	·132	·126	·118
	a	·00119	·00126	·00131	·00138	·00240	·00145	·00148	·00135
	ϕ_1	..	..	..	..	..	..	−1° 13′ 0″	−1° 5′ 0″
	$\phi_0-\frac{\pi}{2}$	..	..	..	..	..	..	−60° 0′ 0″	−62° 0′ 0″
L′=152	f'	·351	·458	·535	·611	·672	·718	·764	·871
	f_2'	·352	·458	·530	·601	·665	·717	·778	·840
	f_1'	·307	·414	·498	·574	·638	·695	·753	·813
	c	·165	·126	·107	·098	·089	·086	·082	·075
	a	·00111	·00116	·00122	·00128	·00130	·00134	·00137	·00139
	ϕ_1	..	−1° 13′ 0″	−1° 0′ 0″	−0° 57′ 0″	−0° 50′ 0″	−0° 44′ 0″	−0° 38′ 0″	−0° 31′ 0″
	$\phi_0-\frac{\pi}{2}$	..	−61° 0′ 0″	−65° 0′ 0″	−27° 20′ 0″	−69° 0′ 0″	−69° 40′ 0″	−70° 20′ 0″	−72° 0′ 0″
L′=100	f'	·360	·450	·550	·630	·690	·770	·820	·890
	f_2'	·352	·465	·555	·637	·708	·770	·841	·897
	f_1'	·336	·463	·546	·628	·697	·760	·823	·890
	c	·090	·0691	·0600	·0541	·0492	·0471	·0460	·0420
	a	·00101	·00106	·00112	·00116	·00120	·00123	·00125	·00127
	ϕ_1	−0° 43′ 0″	−0° 26′ 0″	−0° 17′ 0″	−0° 10′ 0″	−0° 4′ 0″	−0° 2′ 30″	−0° 0′ 0″	+0° 5′ 0″
	$\phi_0-\frac{\pi}{2}$	−68° 30′ 0″	−73° 20′ 0″	−75° 20′ 0″	−76° 30′ 0″	−77° 20′ 0″	−77° 40′ 0″	−0° 78′ 0″	−78° 40′ 0″

As compared with the experimental values f' given in the Table IV., it is seen that the agreement holds as long as c is less than ·06, after which, as c increases, the values of f_1' become too small, or while the values of f_1' continue to diminish as the load and a increase, the experimental values of f' after diminishing till c is about ·1 or ·15 begin to increase again. In order to see how far this law of variation was explained by the theory, it was necessary to find f_2' the values of f' to a second approximation, and before this to obtain the values of c.

Putting, as in equation (124),

$$L=4{\cdot}84\ L',$$

equation (94) gives

$$c = -2{\cdot}059\frac{L'}{K_1}\,;$$

and by equation (150)

$$c = {\cdot}03116(1+{\cdot}1002\,L')^2\frac{n^2L'}{N}e^{{\cdot}0665T_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (153)$$

Equation (153) gives the values of

$$\frac{c}{n^2}.$$

To obtain the value of n *from the experiments*, these values of $\frac{c}{n^2}$ are substituted in the equation for f', retaining the squares of c, which obtained from equations (89) and (85), is

$$f_2' = f_1'(1+5c^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (154)$$

whence, substituting the values of $\frac{c}{n^2}$ obtained from (153) we have

$$f_2' = f_1' + 5\left(\frac{c}{n^2}\right)^2 n^4 f_1'.$$

Therefore, choosing any experimental values of f', and subtracting the corresponding value of f_1' in Table IV., n is given by—

$$n^4 = \frac{f'-f_1'}{5\left(\frac{c}{n^2}\right)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (155)$$

In this experiment irregularities become important, and it has been necessary to calculate several values of n in this way and take the mean, which is

$$n = 1{\cdot}25 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (156)$$

It has been shown (Art. 35) that necking might account for a value of n as great as 1·33, while if there were no necking n would still have a value in consequence of variations of a along the journal.

Substituting this value of n in equations (148 and 153),

$$\left.\begin{aligned} a &= {\cdot}00077(1+{\cdot}002\,L')e^{{\cdot}0222T_m} \\ c &= {\cdot}0487(1+{\cdot}002\,L')^2\frac{L'}{N}e^{{\cdot}0665T_m} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (157)$$

from which equation the values of a and c have been calculated for Table IV. for all values of L′ less than 415 lbs. These are all Mr. TOWER's experiments with olive oil, except those of which Mr. TOWER has expressed himself doubtful as to the results.

The values of c, as given by equation (94) are only a first approximation and are too large, but the error is not large, even when $c={\cdot}5$ only amounting to 8 per cent., as is shown by comparing equation 104 with 95.

With these values of c in the equation (154) the values of f_2' have been calculated for all values of c up to ·250. At $c={\cdot}12$ these values of f_2' are about 5 per cent. larger than the experimental values, but they have been carried to $c={\cdot}25$ in order to show that the calculated friction follows in its variations the idiosyncracies of the experimental frictions, falling with the load to a certain minimum, and then rising again.

These values of f_2' carry the comparison of the frictions deduced from the theory up to loads of 205 lbs. for all velocities, and up to 363 lbs. for the highest velocity. To carry the approximation further use has been made of the more complete integrations of the equations for the case of

$$c={\cdot}5.$$

These are given by equations (104) and (105).

As already stated, comparing (104) with (94) it appears that when $c={\cdot}5$ the approximate values of c in the Table IV. are about 8 per cent. too large; that is to say, a value $c={\cdot}540$ in the table would show that the actual value was $c={\cdot}5$.

Comparing equation (95), from which the values f_1' have been calculated, with equation (105), it appears that when $c={\cdot}5$ the values of f' by (105) are given by

$$f'=\frac{2{\cdot}3773}{1{\cdot}37}f_1'$$

This is not, however, quite satisfactory, as that portion of the friction which is due to necking does not increase with the load. This portion in f_1' is

$$\frac{n-1}{n}f_1'$$

So that for $c={\cdot}5$

$$f'=\frac{2{\cdot}3773+1{\cdot}37(n-1)}{1{\cdot}37n}f \quad \ldots\ldots\ldots\ldots \quad (158)$$

and since $n=1{\cdot}25$, this gives for $c={\cdot}5$

$$f'=1{\cdot}585f_1'$$

If, therefore, any of the approximate values of c were exactly ·540, the complete value of f' would be 1·585 times the value of f_1'. This does not happen, the nearest approximate values of c being ·578, ·520, ·520, ·510. Multiplying the corresponding values of f_1' by 1·585, the results are as follows :—

Tabular. c.	Tabular. f_1'.	1·505 f_1'.	Experimental. f.	Difference.
·578	·36	·57	·58	·01
·520	·414	·656	·65	− ·005
·520	·314	·498	·472	− ·026
·510	·249	·394		

It thus appears that the approximation is very close, the calculated values for the first, in which c is greater than ·540, being too small, and for the rest, in which c was smaller than ·540, too large, which is exactly what was to be expected.

These corrected values of f_1' have been introduced in Table IV. in brackets. As they occur with different loads and different velocities, they afford a very severe test of the correctness of the conclusions arrived at as to the variations of A and T with the load and temperature, also as to the condition expressed by n. Had the values of c and f' been completely calculated as for the case of $c = ·5$, there would have been close agreement for all the calculated and experimental values of f'.

This close agreement strongly implies, what was hardly to be expected, namely, that the surfaces, in altering their form under increasing loads, preserve their circular shape so exactly that the thickness of the oil film is everywhere approximately

$$a(1+c\sin(\theta-\phi)).$$

A still more severe test of this is, however, furnished by the pressure experiments with brass No. 2 in Mr. TOWER's second report.

41. *The Velocity of Maximum Carrying Power.*

The limits to the carrying powers are not very clearly brought out in these recorded experiments of Mr. TOWER, as indeed it was impossible they should be, as each time the limit is reached the brass and journal require refitting. But it appears from Table I. and all the similar tables with the oil bath in Mr. TOWER's reports, that the limit was not reached in any case in which the load and velocity were such as to make c less than ·5. In many cases they were such as to make c considerably greater than this, but in such cases there seems to have been occasional seizing. There seems, however, to have been one exception to this case, in which the journal was run at 20 revolutions per minute with a nominal load of 443 lbs. per square inch with brass No. 2 without seizing, in which case c, as determined either by the friction or load, becomes nearly ·9.

It does not appear that any case is mentioned of seizing having occurred at high speeds, so that the experiments show no evidence of a maximum carrying power at a particular velocity.

This is so far in accordance with the conclusions of Art. (33*a*), for substituting the values of A B C E, as determined Art. (37), it appears by equation (123B) that the maximum would not be reached until T_m, the rise of temperature due to friction, reached 72° Fahr., which, seeing that at a velocity of 450 revolutions T_m is less than 17°, implies that the maximum carrying power would not be reached until the speed was 1500 or 2000 revolutions; notwithstanding $\frac{dL}{dU}c$ constant is very small at 450 revolutions.

This is with the rise of temperature due to legitimate friction with perfect lubrication. But if, owing to inequalities of the surfaces, there is excessive friction without corresponding carrying power, *i.e.*, if n, the effect of necking, is as large as 3 or 4, which it is with new brasses, then the maximum carrying power might be reached at comparatively small velocities; thus suppose $T=13$ when $N=100$ $U=21$, Equation (123B) gives

$$\frac{dL}{dU}=0,$$

or the maximum carrying power would be reached; all which seems to be in strict accordance with experience, particularly with new brasses.

42. *Application of the Equations to* Mr. TOWER'S *Experiments with Brass No.* 2 *to determine the Oil Pressure round the Journal.*

The approximate equation (74) is available to determine the pressure at any part of the journal, *i.e.*, for any value of θ so long as c is small, but these approximations fail for much smaller values of c than for others, for this reason, together with the fact that the only case in which the pressure has been measured c is large, the pressures have only been calculated for $c=\cdot5$, in which the approximations have been carried to the extreme extent.

These are obtained directly from equation (107), and the pressures divided by K_1c are given in Table II., Section VI.

The results of Mr. TOWER'S experiments with brass No. 2 are given in Table XII., Art. 34.

Had the friction been recorded in the experiments in which Mr. TOWER measured the pressures with brass No. 2 as with brass No. 1, the values of c might have been obtained as in the case of brass No. 1. But as this was not done the value of c for these experiments with brass No. 2 could only be inferred from the agreement of the relative oil pressures measured in different parts of the journal, those calculated for the same parts with a particular value of c. This was a matter of trial, and as it was found that the agreement was very close when

$$c=\cdot5,$$

further attempts were not made.

With the section at the middle of the brass the calculated and experimental results are shown in Table V.

TABLE V.—Comparison of Relative Pressures, calculated by Equation (107) when $c = \cdot 5$, with the Pressures Measured by Mr. TOWER, see Table XII., Art. 34, Brass No. 2.

The values of θ measured from middle of arc at which pressures were measured.	Pressure measured at the middle of the journal. Table XII., TOWER.	$\frac{p-p_0}{-K_1c}$ calculated. Table II.	Relative values, experimental.	Relative values, calculated.	$-K_1c$.
$-29^\circ\ 20'\ 20''$	500	·7923	·800	·781	639
$0\ \ 0\ \ 0$	625	1·0150	1·000	1·000	615
$29\ \ 20\ \ 20$	370	·6609	·592	·651	560

This agreement, although not exact, is, considering the nature of the test, very close. The divergence seems to show that in the experiments c was somewhat more than ·5, but it is doubtful if the agreement would have been exact as, owing to the journal having been run in one direction only, it seems probable that the radius of the brass was probably slightly greatest on the *on* side.

Deducing the value of K_1c by dividing the experimental pressure by the calculated values of $\frac{p-p_0}{K_1c}$ the values given in the last column are found. An alteration in the value of c would but slightly have altered the middle value of $\frac{p-p_0}{Kc}$ in the same direction as the alteration of c; hence taking this value, and making $c = \cdot 520$, as being nearer the real value,

$$K_1c = -640 \quad \ldots\ldots\ldots\ldots \quad (159)$$

In these experiments

$$N = 150$$

$$L' = 333 \quad \ldots\ldots\ldots\ldots \quad (160)$$

From equation (104)

$$L = -2 \cdot 5504 \times Kc$$

$$\frac{L}{4} = 408 \quad \ldots\ldots\ldots\ldots \quad (161)$$

therefore

$$s = \frac{L}{4L'}$$

$$= 1 \cdot 21 \quad \ldots\ldots\ldots\ldots \quad (162)$$

To find a

$$\therefore \quad K_1 = -1230$$

by equation (150)

$$=\frac{66{\cdot}08e^{-{\cdot}0666\mathrm{T}_m}}{n^2(1+002\mathrm{L})^2}\mathrm{N}$$

whence

$$a_s^3=000001088e^{-{\cdot}0666\,\mathrm{T}_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (163)$$

and taking T_m the same as with brass No. 1, and olive oil at N=180, *i.e.*, 5·83° Fahr., with brass No. 2, at 70·5° Fahr.

$$\left.\begin{array}{ll} & a_s=00086 \\ \text{instead of with brass No. 1} & \\ & a_s=00077 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (164)$$

The difference in the radii of curvature of the two brasses, the one deduced from the measured friction, the other deduced from the measured differences of pressure at different positions round the journal, come out equal within $\frac{1}{10000}$th part of an inch, and the values of a differing only by 11 per cent. Had the frictions been given with brass No. 2, this agreement would have afforded an independent comparison of the values of a. As it is, the only probability of equality in these two brasses arises from the probability of their having been bedded in the same way.

In deducing the value a for brass No. 2, it has been assumed that the oil, which was mineral, had the same law of viscosity as the olive oil. Both these oils were used with brass No. 1, and the results are nearly the same, the mean resistances, as given by Mr. TOWER, are as 0·623 to 0·654, or the viscosity of the mineral oil being 0·95 that for olive oil; had this been taken into account, the value of a_s for brass No. 2 would have been still nearer that for brass No. 1, being ·00084 as against ·00077.

As the radii of the two brasses seem to be so near, and as the resistance was measured for brass No. 1 under circumstances closely resembling those of the experiment with No. 2, a further test of the exactness of the theory is furnished by comparing the calculated friction with brass No. 2 with that measured with brass No. 1, with the same oil, the same speed, and nearly the same load.

As in equation (158)

$$-f'=2{\cdot}3773\mathrm{K}_2+1{\cdot}37(n-1)\mathrm{K}_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (165)$$

$$-\mathrm{K}_2={\cdot}21\frac{\mu}{a}\mathrm{N}$$

Whence, taking account of the values of μ for mineral and olive oils, and the values of a for brass No. 1 and No. 2 for mineral oil and brass No. 2, K_2 has 0·871 of the value in equation (150)

$$-\mathrm{K}_2=\frac{{\cdot}871\times{\cdot}0034e^{-{\cdot}0443\mathrm{T}_m}}{(1+{\cdot}002\mathrm{L}')n}\mathrm{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (166)$$

which, when $T=5{\cdot}83^\circ$, $N=150$, $L'=337$, $n=1{\cdot}25$, being substituted in equation

$$K_2=-0{\cdot}1665$$

$$f'=4{\cdot}46 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (167)$$

In Mr. TOWER's Table IV., it appears that with brass No. 1, mineral oil,

$$N=150 \qquad L'=310 \qquad f'=4{\cdot}4 \qquad L'=415 \qquad f'={\cdot}51$$

whence interpolating for

$$L'=337$$

$$f'=4{\cdot}58 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (168)$$

This agreement is very close, for taking account of the difference of radius, the calculated friction for brass No. 2 should have been about ·95 of the measured friction with brass No. 2.

In order to show the agreement between the calculated pressures and those of Mr. TOWER, the values of $\frac{p-p_0}{K_1 c}$ for $c={\cdot}5$ have been plotted, and are shown in Plate 8, figs. 2 and 3, the crosses indicating the experiments with brass No. 2, as in Table VII. (TOWER).

43. *Conclusions.*

The experiments to which the theory has been definitely applied may be taken to include all Mr. TOWER's experiments with the 4-inch journal and oil bath, in which the number of revolutions per minute was between 100 and 450, and the nominal loads in lbs. per sq. inch between 100 and 415. The other experiments with the oil bath were with loads from 415, till the journal seized at 520, 573, or 625; and a set of experiments with brass No. 2 at 20 revolutions per minute. All these experiments were under extreme conditions, for which, by the theory, c was so great as to render lubrication incomplete, and preclude the application of the theory without further integrations.

The theory has, therefore, been tested by experiments throughout the entire range of circumstances to which the particular integrations undertaken are applicable. And the results, which in many cases check one another, are consistent throughout.

The agreement of the experimental results with the particular equations obtained on the assumption that the brass, as well as the journal, are truly circular, must be attributed to the same causes as the great regularity presented by the experimental results themselves.

Fundamental amongst these causes is, as Mr. TOWER has pointed out, the perfect supply of lubricant obtained with the oil bath. But scarcely less important must have been the truth with which the brasses were first fitted to the journal, the smallness of the subsequent wear, and the variety of the conditions as to magnitude of load, speed, and direction of motion.

That a brass in continuous use should preserve a circular section with a constant radius requires either that there should be no wear at all, or that the wear at any point P should be proportional to sin (90°−POH).

Experience shows that there is wear in ordinary practice, and even in Mr. **Tower's** experiments there seems to have been some wear. In these experiments, however, there is every reason to suppose that the wear would have been approximately proportional to $c \sin(\phi_0-\theta)=c \sin(90^\circ-\mathrm{POH})$, because this represents the approach of the brass to the journal within the mean distance a, for all points, except those at which it is negative; at these there would be no wear. So long then as the journal ran in one direction only, the wear would tend to preserve the radius and true circular form of that portion of the arc from C to F (fig. 17, p. 193), altering the radius at F, and enlarging it from F to D. On reversal, however, C and F change sides, and hence alternate motion in both directions would preserve the radius constant all over the brass. The experience emphasized by Mr. **Tower** that the journal after running for some time in one direction would not run at first in the other, strongly bears out this conclusion. Hence it follows that had the journal been continuously run in one direction the condition of lubrication, as shown by the distribution of oil pressure round the journal, would have been modified, the pressure falling between O and B on the *on* side of the journal, a conclusion which is borne out by the fact that in the experiments with brass No. 2, which was run for some time continuously in one direction, the pressure measured on the *on* side is somewhat below that calculated on the assumption of circular form, although the agreement is close for the other four points (see fig. 2, Plate 8).

When the surfaces are completely separated by oil it is difficult to see what can cause wear. But there is generally metallic contact at starting, and hence abrasion, which will introduce metallic particles into the oil (blacken it); these particles will be more or less carried round and round, causing wear and increasing the number of particles and the viscosity of the oil. Thus the rate of wear would depend on the impurities in the oil, the values of c, $\frac{1}{a}$ and the velocity of the journal, and hence would render the greatest velocity at which the maximum load could be carried with a large value of c small. A conclusion which seems to be confirmed by Mr. **Tower's** experiments at twenty revolutions per minute.

In cases such as engine bearings the wear causes the radius of curvature of the brass continually to increase, and hence a and c must continually increase with wear. But in order to apply the theory to such cases the change in the direction of the load (or U_1 and V_1) have to be taken into account.

That the circumstances of Mr. **Tower's** experiments are not those of ordinary practice, and hence that the particular equations deduced in order to apply the theory to these experiments do not apply to ordinary cases, does not show that the general theory, as given in equations (15), (18), and (19), could not be applied to ordinary cases were the conditions sufficiently known.

These experiments of Mr. TOWER have afforded the means of verifying the theory for a particular case, and hence has established its truth as applicable to all cases for which the integrations can be effected.

The circumstances expressed by

$$\mu, \frac{L}{U}, \frac{a}{R}, c, \phi_0, \phi_1, n, m, C, A, E, B,$$

which are shown by the theory to be the principal circumstances on which lubrication depends, although not the same in other cases, will still be the principal circumstances and indicate the conditions to be fulfilled in order to secure good lubrication.

The verification of the equations for viscous fluids under such extreme circumstances affords a severe test of the truth and completeness of the assumptions on which these equations were founded. While the result of the whole research is to point to a conclusion (important in Natural Philosophy) that not only in cases of intentional lubrication, but wherever hard surfaces under pressure slide over each other without abrasion, they are separated by a film of some foreign matter whether perceivable or not. And that the question as to whether this action can be continuous or not turns on whether the action tends to preserve the matter between the surfaces at the points of pressure as in the apparently unique case of the revolving journal, or tends to sweep it to one side as is the result of all backwards and forward rubbing with continuous pressure.

The fact that a little grease will enable almost any surfaces to slide for a time has tended doubtless to obscure the action of the revolving journal to maintain the oil between the surfaces at the point of pressure. And yet, although only now understood, it is this action that has alone rendered our machines, and even our carriages possible. The only other self-acting system of lubrication is that of reciprocating joints with alternate pressure on and separation (drawing the oil back or a fresh supply) of the surfaces. This plays an important part in certain machines, as in the steam engine, and is as fundamental to animal mechanics as the lubricating action of the journal is to mechanical contrivances.

V. *Further Observations on Enterochlorophyll, and Allied Pigments.*

By C. A. Mac Munn, *M.A., M.D.*

Communicated by Professor M. Foster, *Sec.R.S.*

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[Plates 9, 10.]

In a paper, read before the Royal Society in 1883,* I described the results of an examination of the so-called "bile" of invertebrates, and proved that the alcohol extracts of the "liver," or other appendage of the intestine answering to it, showed a spectrum so like that of vegetable chlorophyll as to have led me to conclude that no essential difference exists between the spectrum of enterochlorophyll and plant chlorophyll.

At that time I could not decide the points which are now considered.

The object of the present investigation was to determine:—(1) Whether enterochlorophyll is due to the presence of symbiotic algæ or not; (2) whether it is an *immediate* food-product and merely an instance of the intracellular digestion of food chlorophyll; (3) if it is not derived from either of these sources, is it built up by and in the liver of the animal yielding it? (4) in what points does it differ from plant chlorophyll and the chlorophyll of *Spongilla?*

I believe I can prove the absence of symbiotic algæ, the absence of food-products, the animal origin of the pigment, and that it yields, at least in some cases, similar decomposition-products to plant chlorophyll. This evidence is not based on spectroscopic examination only, but also on the study of the morphology of enterochlorophyll and on the absence of starch and cellulose.

At the same time I do not wish to appear too confident as to the purely animal origin of the pigment in *all* cases.

Spectrum of Chlorophyll in a Living Leaf and in an Animal containing Chlorophyll built up by itself.

What is the spectrum of chlorophyll in a living leaf? To enable one to reply to this question a suitable method of examination must be adopted, and I may say at once that the chemical spectroscope is not suited for the examination, (1) because of its greater dispersion, (2) owing to the difficulty of sufficiently illuminating the object. The leaf should be examined by means of the microspectroscope and illuminated by the help of a substage condenser; if necessary a section should be made, or, if the leaf is too thin to show the full spectrum, it may be necessary to place one leaf over another. *In a leaf so examined at least five bands are visible, and it is these five bands, with another nearer the violet, which are seen in an alcohol solution of chlorophyll.* I examined the leaves of thirteen plants in this way successively, and in every one I could see the five bands. The plants taken were:—*Ilex*, *Hedera*, *Agapanthus*, *Lilium*, *Aspidium* (*filix mas*) (frond), *Scolopendrium* (frond), *Begonia*, *Laurus*, *Ficus* (*elastica*), *Seaforthia* (*elegans*), *Geranium*, *Primula*, and common grass.

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* Proc. Roy. Soc., vol. 35 (1883), p. 370.

Hence KRAUS'S* map of the spectrum of a living leaf is correct, and HANSEN'S statement to this effect can be verified. Plate 9, Chart I., spectrum 1, shows this spectrum. If a *Spongilla*, which, as Professor LANKESTER† has shown, is a true chlorophyll-building animal, be examined in the same manner, the bands are found to agree with those of the spectrum of a leaf; such is also the case in an infusorian coloured by its own chlorophyll, *e.g.*, *Ophrydium*, spectra 2 and 3, Chart I.‡

Further, it will be shown that an alcohol solution of *Spongilla* chlorophyll shows the same bands as a similar solution of plant chlorophyll, and closely resembling a similar solution of enterochlorophyll. I have not thought it advisable to mention all recent researches on plant chlorophyll, because they have not yet emerged from a state of confusion and nothing could be gained by doing so. My object is to show that whether what has been named chlorophyll has or has not been isolated, there exists in plants a green colouring matter which, before it has been touched by a reagent, gives the same spectrum as a green colouring matter in an animal, and that the same solutions of both colouring matters give the same spectra, which differ slightly, but in no essential respect, from those of similar solutions of enterochlorophyll.

Before proceeding to describe the results of saponifying vegetable and animal chlorophyll, I will now give the result of an examination of the "liver" pigments of some invertebrate animals.

The "Liver" Pigments of some Invertebrates.

KRUKENBERG and I found, independently of each other, that the alcohol extracts of the "livers" of some animals showed a band in red; he called the pigments giving this band *hepatochromates*, but neither from his description or drawings of the spectra can it be inferred that he knew he was dealing with a true chlorophyll. In my paper, already referred to,[*] I had shown enterochlorophyll to be present in *Ostræa*, *Mytilus*, *Cardium*, *Anodonta*, *Unio*, *Octopus*, *Buccinum*, *Fusus*, *Purpura*, *Littorina*, *Helix aspersa*, *Helix pomatia*, *Helix citrina*, *Arion*, and *Limax* among *Mollusca*. In *Homarus*, *Cancer*, *Carcinus*, *Pagurus*, and *Astacus* among *Arthropoda*. In *Uraster*, *Asterias*, and *Echinus* among *Echinodermata*. A chlorophyll band is seen in KRUKENBERG's drawings[†] of the alcohol extracts of the "livers" of *Grapsus marmoratus*, *Carcinus mœnas*, *Pilumnus villosus*, *Eriphia spinifrons*, *Homarus vulgaris*, *Buthus occitanus*, *Tethys fimbria*, *Pleurobranchus*, *Eledone moschata*, *Aplysia depilans*, and *Mytilus edulis*. It is satisfactory to know that KRUKENBERG has come to the conclusion that his "hepatochromates" are *animal pigments*, and his evidence is of the more value in this case as he has made a great number of observations on animal colouring matters.

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* 'Zur Kenntniss der Chlorophyllfarbstoffe,' &c., 1872. Tafel I., 5.

† In Professor LANKESTER'S early description of *Spongilla* chlorophyll he called it chondrichlor, but subsequently he agreed with SORBY as to the identity of this colouring matter with plant chlorophyll. See also his paper in Quart. Journ. Micro. Soc., vol. 22 (1882), pp. 229–254.

‡ I was not certain about the fourth band, and so have left it out of the drawing of this spectrum.

As I have gained more experience in the examination of solutions since my last paper was communicated, I may have to describe in this the spectra of some already referred to, especially as differences are sometimes seen when a great number of the same species is examined; this remark applies more especially to starfishes, in which the chlorophyll obtained from the radial cœca shows certain differences with regard to the dominant band, which, in my opinion, establish beyond all doubt the animal origin of the pigment. Besides, with the large spectroscope obtained with the grant allowed me by the Royal Society, I am able to measure more accurately the wavelengths of the bands than I could before.[‡] The consideration of the spectra of solutions of vegetable chlorophyll should naturally precede that of those of animal chlorophyll, but it will be deferred for convenience until I come to describe the results of saponification.

MOLLUSCA.

Paludina vivipera.—In a deep layer of the rectified spirit extract[§] of the "liver" of this species the three bands shown in spectrum 4, Chart I., are seen, and in a thinner layer another band between green and blue. The solution was a deep-yellow colour and fluoresced red. Its first three bands read approximately:—1st, λ 678 to λ 656; 2nd, λ 620 to λ 600; 3rd, λ 552 to λ 539. With nitric acid the change already described, and to be referred to below, took place. Hence the enterochlorophyll present differs in no respect from that of other mollusca.

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[*] *Loc. cit.*

[†] "Vergleichend-physiologische Studien," 3te Abth. 1880. Taf. 1. KRUKENBERG, too, arrived at the same conclusion as myself, namely, that various pigments are prepared in the liver for use elsewhere (S. 189), especially for the integument.

[‡] The bands in blue and violet are most difficult to measure, and if with even better instruments they are found to differ from my measurements the fault, I hope, will not be attributed to inaccuracy.

[§] Of course this and all the following extracts were filtered before examination.

Limnæus stagnalis.—The method pursued in this case, and in all the following, was the same, and differs from that described in my former paper, the "liver" or other enteric appendage answering to it being extracted for some hours with the solvent, the extraction being generally repeated if necessary; by the adoption of this method a greater quantity of colouring matter is got into solution.

Rectified spirit extracts of the "liver" are greenish-yellow and show a red fluorescence; the spectrum consists of five bands, which differ slightly in position from those of an absolute alcohol extract, the spectrum of which is shown in spectrum 5, Chart I. The bands read as follows:—1st, from λ 678 to λ 651·5; 2nd, λ 618 to λ 600; 3rd, λ 547 to λ 537; 4th, (about) λ 519 to λ 503; and 5th, (about) λ 492·5 to λ 473·5. On adding nitric acid the colour became greener, and the bands assumed the position shown in Chart I., spectrum 6, their centres reading:—1st, λ 654; 2nd, λ 602·5; 3rd, λ 570·5; 4th, λ 536; and 5th, uncertain. If allowed to stand longer in contact with the acid the fluid assumed a bluish tint.

Caustic soda seems to affect the position of the bands,* the colour of the solution remaining green, an alcohol solution so treated gave a spectrum whose bands read as follows:—1st band, λ 683·5 to λ 657; 2nd, λ 625 to λ 602·5; 3rd, λ 551 to λ 538·5; 4th, λ 521·5 to λ 498·5 (?). No noticeable shifting of the bands took place with acetic acid. An aqueous extract of the "liver" also gives a chlorophyll-like spectrum. In some parts of the body of this mollusc there is evidence of the presence of hæmoglobin, and in its black parts and elsewhere a lutein or lipochrome. As will be shown further on, the 4th and 5th bands of the enterochlorophyll spectrum belong to a similar pigment. I could find no enterohæmatin in the "liver" of this species.

Trochus ziziphinus.—The absolute alcohol extract of the "liver" is green, fluoresces red, and shows spectrum 7, Chart I., the band reading as follows:—1st band, λ 672 to λ 651·5; 2nd, (about) λ 618 to λ 593; 3rd, λ 548·5 to λ 535; 4th, uncertain. With nitric acid the colour became greener, and the usual series of bands appeared.

Trochus cinerarius.—An absolute alcohol extract of the "liver" is yellow, fluoresces red, and shows spectrum 8, Chart I. The bands reading as follows:—1st, λ 678 to λ 657 (light shading up to 647); 2nd, λ 620·5 to λ 595; 3rd, λ 545·5 to λ 535; 4th and 5th, from about λ 519 to λ 484·5 (?). It became greener with nitric acid, and showed the same band as in other cases. Caustic soda intensified the double band nearer violet

Littorina littorea.—Although I have described the "liver" pigments of this mollusc in my former paper, I have made some further experiments on them which are worth recording. An absolute alcohol extract of the "liver" is greenish-yellow, and gives a well-marked red fluorescence; the fully developed spectrum is shown in spectrum 9, Chart I., the three principal bands of which read as follows:—1st, λ 678 to λ 654; 2nd, λ 623 to λ 600; 3rd, λ 548·5 to λ 537. On treating with caustic soda a turbidity was produced; on filtering, evaporating, and extracting the residue with petroleum ether[*] the solution was green and showed a red fluorescence; and now a dark band was seen to replace the 4th and 5th bands of spectrum 9, which extended from λ 496·5 to λ 477, another was perhaps also visible in the violet. On evaporating this solution down, and extracting with bisulphide of carbon, a deep yellow solution was obtained showing similar bands, the two nearer violet being plainly marked, the first much darker than the second, and reading λ 524·5 to λ 503, and λ 492·5 to λ 473·5.

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* It also weakened the fluorescence. In the case of *Mytilus* and *Ostræa* I did not notice any change with NaHO.

The residue was also soluble in ether and in chloroform. Hence the enterochlorophyll of *Littorina* thus treated is soluble in alcohol, ether, petroleum ether, chloroform, and bisulphide of carbon. It is soluble in the solvents of the "lipochromes," and of fat, and this agrees with the microscopic characters of enterochlorophyll, for it is often dissolved in oil globules, as will be shown further on. According to my own observations[†] a lutein pigment is present in *Littorina*, and KRUKENBERG[‡] finds the same which he calls a lipochrome, and which I have no doubt is prepared in the "liver." But there is another interesting point about *Littorina:* the pharyngeal muscle yields hæmoglobin, and if the "liver" be examined in the compressorium with a substage condenser and SWAN lamp a spectrum is seen which is shown in spectrum 10, Chart I.; now, these bands recall to mind hæmochromogen, or what I have called enterohæmatin. An aqueous solution of the "liver" treated with ammonium sulphide shows these bands intensified, so that they are at least closely related to hæmatin; moreover, in other parts of the body of this species, histohæmatins are found, hence it is highly probable that in the "liver" the radical of these pigments is prepared just as the lipochrome radical is also prepared in it. That this hæmatin pigment is related to enterochlorophyll is very probable.

Patella vulgata.—Absolute alcohol extracts of the "liver" are yellowish-green and fluoresce red. The spectrum of an alcohol solution is shown in spectrum 11, Chart I., the bands reading:—1st, λ 678 to λ 654; 2nd, λ 620·5 to λ 598; 3rd, λ 547 to λ 536. The double band extended from λ 521·5 to λ 475 (?). On adding nitric acid the usual series of bands appeared, reading:—1st, λ 669 to λ 649; 2nd, λ 613 to λ 595; 3rd, λ 580·5 to λ 569, and 4th, λ 545·5 to λ 537 (?). Acetic acid did not appear to affect the colour or spectrum much. Caustic potash acted as in most other cases, *i.e.*, intensifying the bands nearer violet. Sulphuric acid produced the same effect as nitric; so also did hydrochloric. But, besides enterochlorophyll, *Patella* often shows the presence of enterohæmatin in its "bile." On removing the animal from its shell, the blackish membrane covering the visceral mass is seen to be more prominent posteriorly to the right tentacle; if this part be punctured, a brownish viscid fluid exudes, which examined quickly shows two hæmochromogen-like bands, which disappear on exposure to air, and reappear with ammonium sulphide (Chart I., spectrum 12).

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[*] This shows that this enterochlorophyll is changed by caustic soda, and also that its *yellow* constituent is changed by it.

[†] Proc. Birm. Phil. Soc., vol. 3 (1883).

[‡] "Grundzüge einer vergleichenden Physiologie der Farbstoffe und der Farben," 1884.

In *Patella*, the pharyngeal muscles contain hæmoglobin (Ray Lankester), and histohæmatins occur in various parts of the body; therefore, the same remarks made about the "liver" pigments of *Littorina*, will apply here. Lutein (=a lipochrome) can also be detected in various parts, as well as in the "liver."

Helix pomatia.*—From the "liver" of this mollusc, pigments are obtainable which differ in no essential respect from those of other pulmonate mollusca, they have been described by me in a former paper. I have made a few further observations since, which are as follows:—A solution of the "liver" pigments in weak alcohol is greenish-yellow, fluoresces red, and gives spectrum 13, Chart I., of which the bands read:—1st, λ 672 to λ 660, feeble shading to λ 647; 2nd, λ 623 to λ 593; 3rd, λ 561·5 to λ 557; 4th, *about* λ 545·5 to λ 529·5. There was also a fifth band, *perhaps* λ 494·5 to λ 475. A second extraction with absolute alcohol showed a spectrum belonging to enterochlorophyll only (spectrum 14, Chart I.). The red fluorescence of this green extract was well marked, and its bands read:—1st, λ 672 to λ 657, shading to λ 649; 2nd, λ 620·5 to λ 596·5 (?); 3rd, λ 545·5 to λ 532; and 5th, λ 490·5 to λ 472 (?). In the absolute alcohol extract of another "liver," spectrum 15, Chart I., was observed, which differs from both of the above extracts; these bands read as follows:—1st, λ 672 to λ 657, shading to λ 647; 2nd, λ 623 to λ 593; 3rd, λ 569 to λ 557 (?); 4th, λ 563 to λ 551, and a feeble 5th, λ 494·5 to λ 475. All these solutions were united and saponified, the results will be described further on. Probably spectrum 15 belongs to a colouring matter *intermediate* between enterohæmatin and enterochlorophyll.

Krukenberg† found evidence, as he thought, of the presence of several pigments, but the appearances can probably be explained on the above supposition. I have repeated my former experiments on other Mollusca whose "liver" pigments I have already described, but have nothing further to add to former descriptions.

The Enterohæmatin of Invertebrates.

According to Krukenberg† the change produced by sulphide of ammonium (on enterohæmatin) is not due to a reduction but to the action of an alkali on this pigment, which he names "helico-rubin," but sulphuretted hydrogen and neutral reducing agents produce the same effect; and *if the "bile" of an animal containing*

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* The red bile shows *without any treatment* two enterohæmatin bands:—1st, λ 569 to λ 555; and 2nd, *perhaps* λ 540 to λ 524·5. Hence the idea of Krukenberg, that they only appear when alkalies are added, is not correct.

† *Loc. cit.* See also Sorby's paper on "The Evolution of Hæmoglobin," Quart. Journ. Micro. Soc., vol. 16 (1876), p. 77. Krukenberg apparently did not know of this paper, or he could not have fallen into the error noted above. See also my paper, *loc. cit.*

enterohæmatin be examined quickly, the two bands of the reduced pigment can be seen; on exposure to air they fade away, to be again brought back by reducing agents. Caustic alkalies, no doubt, also cause the bands to appear, but this is no argument against reduction and oxidation. The impropriety of calling this pigment "helicorubin" is patent when we consider that it is not limited to *Helix*, but occurs in *Limax*, *Arion*, *Astacus*, and *Patella*, &c., as has been shown by me. I have tried to convert it into hæmatoporphyrin, but hitherto with only partial success; but I had not enough material to work upon. It is a very unstable body, resembling in this respect Professor LANKESTER'S chlorocruorin. As I have already said, it is probably the mother-substance of those histohæmatins, which are found in animals in whose "livers" it is built up. Another view might be held, namely, that it is an excretion and represents the form in which the above colouring matters are got rid of, but its very instability is against that view.

ECHINODERMATA.

It will be seen that the dominant band of chlorophyll in solutions of the radial cœca of starfishes is sometimes replaced by two narrow ones[*] in the same part of the spectrum; I believe this has been noticed among plants in the case of very young green leaves, but I am unable to find the reference to this statement. It would seem to show that, as an examination of a considerable number of the same species teaches, one meets with enterochlorophyll in all stages of manufacture; in some cases immature and having just been formed, or in stages of preparation; in other cases fully formed, when it more nearly approaches the condition of plant chlorophyll.

Solaster papposa and other species.—The first specimen examined was a brilliant red colour, which colour was due to a pigment having a close resemblance to zoonerythrin (=tetronerythrin), but in thin layers of its solutions showing two or three bands like those of lutein. Hence the pigment cannot be *rhodophan*[†] or *xanthophan*, and its colour shows that it is not *chlorophan*, so that all one can say is that it is a lipochrome.[‡] A rectified spirit extract of the radial cœca (which were brownish) was yellow, had a faint red fluorescence, and gave a well-marked chlorophyll spectrum (spectrum 16, Chart I.). The three most prominent bands read as follows:—1st, λ 669 to λ 651·5; 2nd, λ 618 to λ 593 (?); and 4th, λ 509 to λ 490·5 (?). These measurements are doubtful owing to the small amount of pigment in solution.

The dominant band in red was found in a fourteen-rayed red *Solaster papposa*, slightly different from the above, from λ 672 to λ 651·5 (*i.e.*, in an absolute alcohol solution of the cœca). Its other bands agreed closely with those of the first specimen. Both solutions on treatment with nitric acid gave the usual series of bands. In a twelverayed *Solaster* the dominant band of an absolute alcohol solution of the radial cœca—which was yellow and fluoresced red—extended from λ 669 to λ 657. Other specimens were examined with the same result, their radial cœca furnishing only a small amount of enterochlorophyll. No enterohæmatin could be detected; and in none of their integuments was hæmatoporphyrin found. A full account of the integumental colouring matters is reserved for another communication.

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[*] This double band in red was noticed also in other cases, *e.g.*, *Octopus* and *Anodonta*, &c.

[†] See below.

[‡] See below. Note the one-banded lipochrome in spectrum 16.

Uraster rubens.—A great number of this species have been examined, and the results obtained are so important in deciding the question as to the animal origin of enterochlorophyll, that I think it necessary to give the results in greater detail than in other cases.

(1) *Uraster* with a nodulated integument.—A filtered alcohol extract of the cœca was a dull sap green, and showed a red fluorescence and two well-marked bands, and a feeble third in a deep layer; also in a shallow layer an ill-defined band at the blue end of green. The bands read:—1st, λ 669 to λ 640; 2nd, λ 620·5 to λ 591. With nitric acid the spectrum changed, and the bands read:—1st, λ 665 to λ 640; 2nd, λ 618 to λ 591; 3rd, λ 579 to λ 557 (?). The great breadth of the band in red is here noticeable.

(2) *Uraster* with a red integument.—Here the alcohol extract of the radial cœca was greenish, fluoresced red, and gave the same kind of band in red as (1), but after this solution had stood twelve hours *the band in red could be no longer seen*, and the colour of the solution had changed to orange-yellow. The residue left after evaporation of the alcohol was a pale, yellowish-brown colour, and dissolved in chloroform showed one faint band in the blue part of green. *Hence it would appear that the enterochlorophyll in this case spontaneously changed into another colouring matter;* the amount of material was, however, too small to enable me to determine what this colouring matter was.

(3) A violet *Uraster*.—The radial cœca yielded when extracted with alcohol a deep gamboge-yellow coloured solution, showing a badly-marked band in red, corresponding in position with the above-mentioned band, but showing a strong absorption of the violet end of the spectrum up to E. In a thin layer a broad ill-defined shading from λ 516 to beyond λ 475 became detached. On adding nitric acid a distinct blue colour was produced, the band in red moved nearer the violet, and the broad shading could be no longer seen. Caustic soda did *not* cause this shading to disappear. There is no doubt that these cœca contained a colouring matter which belongs to the lipochromes, and I believe it is more like KÜHNE's rhodophan or xanthophan than anything else. Now, as we find in the integument a similar pigment, there can no longer be a doubt that the integumental pigment (as I formerly showed) is prepared in the radial cœca.

(4) A reddish-brown *Uraster*.—The radial cœca when extracted with alcohol furnished a dark-yellow solution with a red fluorescence. This showed spectrum 17, Chart I., the result of combining the spectrum of a deep and shallow layer. The bands read:—1st, λ 667 to λ 649; 2nd, λ 611 to λ 593; and 3rd, λ 541·5 to λ 529·5.

There was a 4th band, which, after adding caustic soda, became more distinct, and read about λ 505 to λ 484·5 (?).

(5) The cœca of a brown *Uraster* were also extracted with absolute alcohol, the extract added to that obtained from the cœca of (4), and saponified by HANSEN'S method. The extract from the cœca of (5) agreed in its spectrum with that of (4). The result of this experiment will be described under "*Saponification.*"

(6) An orange and brown specimen of *Uraster.*—The dirty green radial cœca were extracted with absolute alcohol, and furnished an orange-coloured solution with a red fluorescence, which showed a spectrum similar to 17, Chart I. The bands read approximately: 1st, λ 667 to λ 651·5; 2nd, λ 615·5 to λ 593; 3rd, λ 543 to λ 532 (?), and a 4th, about λ 511·5 to λ 486·5.

(7) A brown *Uraster,* with greenish cœca.—These formed in absolute alcohol a yellow solution with a greenish-brown tinge and a red fluorescence. The bands read: 1st, λ 669 to λ 647; 2nd, λ 613 to λ 593; 3rd, λ 540 to λ 530·5. The 4th band could not be read distinctly, but appeared to be λ 511·5 to λ 475 (?), probably formed by the coalescence of two bands.

If any of these last three solutions were treated with nitric acid it became greenish, and the bands read: 1st, λ 660 to λ 640; 2nd, λ 609 to λ 589; 3rd, λ 576 to λ 557; 4th (perhaps), λ 540 to λ 524·5, and possibly another, λ 505 to λ 484·5.*

The action of zinc and sulphuric acid was tried on these last three solutions, but the result obtained showed that no reduction-products similar to those obtained from hæmatin could be found; nor, indeed, in the case of vegetable chlorophyll could I succeed in getting anything different. Hence the statement that chlorophyll yields similar decomposition-products to hæmatin is erroneous.

(8) An orange *Uraster* with brownish-green cœca.—These extracted with absolute alcohol formed a yellow solution, with a red fluorescence, the bands of which read as follows: 1st, λ 667 to λ 649; 2nd, λ 615·5 to λ 593; 3rd, λ 544 to λ 532, and 4th, about λ 516 to λ 488.

A second extraction of the cœca of the last three specimens furnished the same results on examination, the solutions in absolute alcohol being greenish, with a red fluorescence, the bands reading: 1st, λ 667 to λ 649; 2nd, λ 611 to λ 593; 3rd, λ 543 to λ 529·5, and 4th, λ 516 to λ 488 (?).

A third extract gave the same results; hence it is evident that the only pigment which could be extracted by absolute alcohol was enterochlorophyll.

(9) A brown *Uraster* yielded similar results, the bands of the solutions of the radial cœca corresponding with the above.

While these nine *Urasters* all contained a colouring matter whose bands in alcoholic solutions agree closely enough when allowance is made for the difficulty of measuring the edges of the feeble bands, the following two showed certain peculiarities with regard to the dominant band in red.

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* A second and third extraction of these cœca yielded the same spectra as the above, and these extracts were used for saponifying, as described further on.

(10) A *Uraster* of a brown and orange colour had its cœca extracted with absolute alcohol. The solution obtained was a deep yellow, with a red fluorescence, and gave spectrum 18, Chart I., which is the result of combining the spectrum of a deep and shallow layer. The bands read as follows: 1st, λ 683·5 to λ 675; 2nd, λ 664 to λ 651·5; 3rd, λ 613 to λ 593 (?); 4th, λ 545·5 to λ 532 (or λ 543 to λ 529·5), and the 5th, about λ 505 to λ 473·5. I could not see any other band nearer violet. That this spectrum did not belong to chlorofucin was seen by the action of caustic soda on it, as the bands were hardly affected, whereas in a similar solution of chlorofucin they become completely changed under the influence of this reagent.

On treatment with nitric acid the similarity in constitution of this pigment to other enterochlorophylls was proved, although the bands are not coincident; they read: 1st, about λ 681 to λ 669; 2nd, λ 660 to λ 645; 3rd, λ 609 to λ 589; the others were uncertain. On evaporating on the water-bath, a yellowish residue with particles of a brown colour in it, was obtained, and on extracting with petroleum-ether and filtering, a yellow solution was obtained giving *two bands* in the red, with these readings: 1st, λ 683·5 to λ 672; 2nd, λ 665 to λ 654; also a broad shading between green and blue. The two former being of equal intensity, and nearly equal breadth. This is shown in spectrum 19, Chart I. On diluting with more petroleum-ether a band became detached from about λ 501 to λ 481. Now according to HANSEN "chlorophyll green" is insoluble in petroleum-ether, but this chlorophyll was soluble in it. In a still more dilute solution (of petroleum-ether) another band, nearer violet, from about λ 467 to λ 451, could be seen. On touching the dried residue with a solution of iodine in iodide of potassium it showed a reddish tinge; with nitric acid it became green, and with sulphuric acid green. On dissolving some residue left after evaporation of a petroleum-ether solution in bisulphide of carbon a reddish-yellow solution was obtained showing only *one* broad band in green and blue.

(11) The cœca of another *Uraster* on being extracted with absolute alcohol yielded a deep-yellow solution with a red fluorescence, and a similar spectrum to that just described, the bands of which read: 1st, λ 683·5 to λ 675; 2nd, λ 665 to λ 651·5; 3rd, λ 613 to λ 593; 4th, λ 543 to λ 529·5; and 5th, λ 505 to λ 475 (?). An attempt was made to get reduction-products from this solution with zinc and sulphuric acid, but with a negative result.

(12) A brown *Uraster*.—The cœca, extracted with absolute alcohol, yielded a deep-yellow solution having a red fluorescence. The bands read: 1st, λ 667 to 651·5; 2nd, λ 615·5 to λ 593; 3rd, λ 545·5 to λ 535; and another from about λ 509 to λ 484·5. I failed to get a reduction-product from this by treating with magnesium and acetic acid.

(13) The deep-yellow solution of the cœca of another *Uraster*, fluoresced red, and

gave the following bands: 1st, λ 667 to λ 649; 2nd, λ 615·5 to λ 593; 3rd, λ 543 to λ 532; and 4th, λ 509 to λ 484·5.

(14) Another solution of the same kind, of the same colour, and with the same bands in its spectrum, was united with that of (13) and saponified by HANSEN'S method, as will be described further on.

Other specimens were examined with the same result, and the presence of one lipochrome or lutein band was found to be the rule, which fact alone goes far to show that the enterochlorophyll of *Uraster rubens* is not a *vegetable* chlorophyll, and the saponification method tends to support this view.

I formerly stated* that among worms I failed to find enterochlorophyll, and I have recently examined the "bile" of *Aphrodite aculeata* with a negative result.

"Bile" of Aphrodite aculeata.†—I find that the stomach of *Aphrodite* contains in its wall hæmoglobin; its presence in the nerve ganglia (of abdomen) had been previously detected (LANKESTER). Although the "bile," which was of a dark-brown colour, did give a faint band in red, yet on evaporating it to dryness and extracting with alcohol a colourless and bandless solution was obtained. Chloroform hardly took up anything from the same residue, being only faintly yellow. Ether, and acetic ether, also failed to extract any colouring matter. It did not contain enterohæmatin. It was but little changed by nitric or sulphuric acid. It contained only a brown pigment, insoluble in alcohol, ether, chloroform, and acetic ether, soluble in water, and unaffected by acids or alkalies.

The Saponification of Vegetable Chlorophyll.

KÜHNE ‡ applied the saponification method to the isolation of the *chromophans* of the retina and succeeded in separating out three pigments from the soap,—chlorophan, rhodophan, and xanthophan,—which he designated the "lichtbeständige" colouring matters of the retina. He showed their points of difference from the lutein of the *corpora lutea* and from yolk pigments and other bodies which hitherto had been known as luteins. It is unnecessary here to describe his results in detail except to mention that these pigments agree in showing SCHWALBE'S iodine reaction when in the *solid* state, *i.e.*, a green-blue to blue with iodine in iodide of potassium, they also become a dark green-blue to blue with concentrated sulphuric or nitric acid,§ and they are soluble in the lutein solvents. KÜHNE has, however, more recently found that when the pigments are pure they may fail to show these colour reactions. Hence all we have to rely on is the presence of certain faint bands in the violet and blue parts of the spectrum and peculiarities of solubility when we wish to determine the presence of such pigments. I have myself repeatedly found that colouring matters giving similar

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[*] *Loc. cit.*

[†] *Cf.* KRUKENBERG, *loc. cit., infra.*

[‡] "Untersuchungen aus dem Physiologischen Institute der Universität zu Heidelberg," Band 1, Heft 4, 1878, and Band 4, Heft 3, 1882. ("Ueber lichtbeständige Farben der Netzhaut," &c.)

[§] CAPRANICA, "Archiv für Anatomie und Physiologie," 1877, Heft 3, S. 285, and SCHWALBE, "Handbuch der gesammten Augenheilkunde," Leipzig, 1874.

spectra to the chromophans individually, and which Krukenberg has assumed to be identical with the chromophans, failed to give any blue coloration with iodine in iodide of potassium, and their reactions with sulphuric and with nitric acid were equally unsatisfactory.

Krukenberg,[*] taking Kühne's researches as a basis, has proposed that all those animal pigments which are soluble in certain solvents, which give bands in the blue and violet parts of the spectrum, and the above reactions when in the solid state, should be included under one name, that of the lipochromes. He has found these lipochromes widely distributed through the animal kingdom. In his early publications he restricted the term to the luteins, but he now includes zoonerythrin (= tetronerythrin). But it seems to me that this generalisation is too great, and that the abandonment of the old term lutein is likely to lead to confusion. However Krukenberg deserves great credit for having evolved order out of chaos, and whether we accept the name lipochromes or not, will matter little if it be kept in mind that they are mostly all lutein-like pigments.

In most cases Krukenberg applied Kühne's saponification method to the isolation of the lipochromes, and found that they "withstand" heating with caustic soda; but I cannot altogether agree with this, because in some cases bands previously invisible come into view, and in many cases bands are much intensified, showing a decided change in the composition of the pigment.

Dr. Adolph Hansen[†] applied the same method to the chlorophyll of young wheat plants, and was led to some important conclusions as to the composition of chlorophyll; he says he has restored to Kraus[‡] the right of having been the first to show how to separate chlorophyll into its constituents.

I need not describe the preliminary treatment to which he subjected his plant-material, but limit myself to the description of the saponification.

The alcohol extract of the leaves is concentrated by evaporation, and the concentrated extract treated when boiling drop by drop with caustic soda solution; when the alcohol has evaporated water is added, and the solution heated again. After the evaporation of the greater part of the water alcohol is again added and the saponification ended. When the alcohol has gone chloride of sodium is added in excess to ensure the separation of the soap. The green soap is now extracted in the separating funnel with petroleum-ether, the extraction being repeated as long as the petroleum-ether appears yellow. The soap is then shaken with pure ether, after which it is extracted with ether containing "some cubic centimetres" of alcohol which extracts the green constituent. In this way the two colouring matters composing chlorophyll are separated from each other, and these Hansen calls "chlorophyll yellow" and "chlorophyll green." The former goes into the petroleum-ether, from which it can be obtained in the form of *yellow needles* on evaporation, or on dissolving the residue in alcohol and evaporating. The latter is obtained purer by extracting the residue obtained by evaporation of the alcohol-ether solution, with alcohol holding ether, whereby salt and other impurities remain behind. According to Hansen "chlorophyll yellow" is a lipochrome,* since it gives the reactions of these pigments with nitric and sulphuric acid and iodine, and the spectrum consists of three bands in the blue half of the spectrum.

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[*] 'Vergleichend-physiologische Studien,' 1880–1882, and 'Grundzüge einer vergleichenden Physiologie der Farbstoffe und der Farben,' 1884; also 'Grundriss der med.-chem. Analyse,' 1884.

[†] 'Arbeiten des botanischen Instituts zu Würzburg,' Bd. 3, Heft i., and 'Verhandlungen der physikalisch-medizinischen Gesellschaft zu Würzburg,' N. F., Band 18, (1884), p. (109). See "Nature," vol. 30, p. 224.

[‡] 'Zur Kenntniss der Chlorophyllfarbstoffe und ihrer Verwandten,' Stuttgart, 1872.

"Chlorophyll green" in alcohol and ether possesses four bands in the red half of the spectrum, one between B and C, covering C in one edge, one between C and D nearer D, one just after D, and the last between D and E nearer E, while the blue half of the spectrum is absorbed from before F onwards to the violet end. It crystallises in sphere-crystals out of the ethereal solution, showing a black cross with polarised light.

Hansen maintains that by this treatment the originally existing chlorophyll green is not decomposed.† But I cannot quite agree with this statement. I find the spectrum of "chlorophyll green" after saponification and when dissolved in ether-alcohol solution not quite the same as before saponification; *it is quite different.*

I now proceed to describe the results of my own experiments. I shall first describe the saponification of vegetable chlorophyll.

Experiments on the Saponification of Vegetable Chlorophyll.

I have not attempted in all these cases to follow up the purification of the pigments so as to obtain them crystallised, my object being to determine the *spectra* of the various solutions and compare them with solutions of animal chlorophyll. In some however I saw both sphere-crystals and needles, and can verify the accuracy of Hansen's descriptions. I will select two sets of experiments to illustrate what I have got to prove, as I find the appearances in most cases coincide with those to be described.

On extracting the green leaves of *Primula* with absolute alcohol after crushing them in this solvent, a green solution with a blood-red fluorescence is obtained in which the bands in the red half* of the spectrum read as follows: 1st band, λ 678 to λ 640; 2nd, λ 627 to λ 600; 3rd, λ 593 to λ 569; then *another band in the green, faint, whose presence can be detected in a living leaf.* To take its wave-length a deeper solution is examined, when we get for the whole series of bands: 1st, λ 681 to λ 638; 2nd, λ 629 to λ 600; 3rd, λ 593 to λ 566; 4th, λ 551 to λ 532; while in a more dilute solution: 5th, λ 486·5 to λ 467; and 6th (about), λ 451 to λ 438. This solution was saponified with caustic soda and the subsequent treatment carried out as in HANSEN's method. (*Supra.*)

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* Prof. Sachs told Dr. Hansen that Millardet had observed similar crystals. Hansen, *loc. cit.* Hartsen, Chem. Central-Blatt, 1872, S. 525, 1875, S. 613, also obtained a yellow crystalline body from Chlorophyll. He also "saponified" chlorophyll. 'Neue Chemische Untersuchungen,' Nordhausen, 1875.

† This statement is in contradiction to the statements of such experienced investigators as Professors Stokes, Sorby, and others. It has been long known that even the small amount of acid in some leaves will decompose chlorophyll, and such violent treatment as boiling with caustic soda must certainly *change* it, as is the case. (*Cf.* also Russell and Lapraik, Journ. Chem. Soc., vol. 41, p. 338, and Sachsse 'Die Chemie und Physiologie der Farbstoffe, Kohlehydrate und Proteinsubtanzen,' 1877.)

The petroleum-ether solution of the soap was yellow, had no fluorescence, and showed two bands: the first from λ 488 to λ 468, and second (about) λ 458·5 to λ 445. If we now examine the mother liquid from which the petroleum-ether, the ether, and the ether with alcohol have removed their pigments, we find that it no longer shows the original spectrum. While the original solution showed in a deep layer spectrum 1, Chart II., this solution showed spectrum 4, Chart II.; hence saponification has altered the chlorophyll to a certain extent. The first ether-alcohol extract of the green soap was only pale-green, but the second was a fine blue-green solution, *with a splendid blood-red fluorescence,* and now gave spectrum 5, Chart II., the bands of which read: 1st, λ 651·5 to λ 627; second, λ 607 to λ 583·5; third, λ 537 to λ 524·5. There is also a feeble band between D and E, such as HANSEN describes from λ 572 to λ 557 (?). On now comparing these bands with those of the original solution they are seen to be *quite different.* In a deeper layer of solution they occupied the following positions: 1st, λ 656 to λ 620·5; 2nd, λ 609 to λ 580·5; 3rd (a shading only), λ 572 to λ 557; and 4th, λ 537 to λ 519.

The action of nitric acid on this isolated "chlorophyll green" did not cause the same bands to appear as in an ordinary alcohol solution of chlorophyll, when treated with this reagent; the spectrum obtained is shown in spectrum 6, Chart II., the colour of the solution being bluish. After some time the band at D, and that after it, became much fainter, the first and fourth bands being very distinct. On comparing this result with that obtained in the case of enterochlorophyll a difference is apparent. I found that the solid "chlorophyll green" went into bisulphide of carbon; but in this the red fluorescence was not so apparent, and as none of this residue went into petroleum-ether there could not have been a lipochrome present. On evaporating a solution of chlorophyll green, and examining with a ⅛th objective, thousands of round green granules were seen; some of these were red in certain lights, and were therefore dichroic, which is a property of the solid pigment, according to HANSEN.†

If grass-chlorophyll is saponified, some *trifling* differences between the spectra of its solutions and those just described are noticed. An absolute alcohol solution prepared in the usual way gives spectrum 7, Chart II., in a deep layer, and spectrum 8, Chart II., in a shallow one. The solution was a brilliant green, with a blood-red fluorescence, and its bands read as follows: 1st, λ 679·5 to λ 636; 2nd, λ 627 to λ 600; 3rd, λ 593 to λ 566; 4th, λ 551 to λ 532; and in a thinner layer: 5th, λ 486·5 to λ 467; 6th, λ 451 to λ 438 (?). I found *that caustic soda alone certainly affected these bands*; that before D could no longer be seen, and the whole spectrum appeared as shown in spectrum 9, Chart II.* The band in red had completely changed its position, as it now read from λ 662·5 to λ 627, and blended into the second band; 3rd, λ 582 to λ 560; 4th, λ 537 to λ 519; moreover the red fluorescence was no longer as noticeable as before. The change brought about, with regard to the position of the bands, is somewhat similar to that caused by nitric acid; thus the alcohol solution of the above chlorophyll on treatment with nitric acid gave: 1st band, λ 665 to λ 640; 2nd, λ 615·5 to λ 593; 3rd, λ 579 to λ 560; 4th, λ 543 to λ 519, the fluorescence being also much diminished. I also found that acetic acid moved the edge of the principal chlorophyll band *towards red*, not, as is usually stated, towards violet—a change which is often seen in solutions of enterochlorophyll. Thus the darkest part of the band is λ 703 to λ 665, and then a shading λ 665 to λ 645.† Ammonia diminishes‡ the red fluorescence. The above results show that there is yet much to be learned about the chlorophyll of plants, and that the saponification process is not quite as harmless towards chlorophyll as recent writers would have us believe. On saponifying and agitating the soap with petroleum-ether a yellow solution was obtained, which gave *three* bands in the violet half of the spectrum, spectrum 10, Chart II., the third band being only visible by daylight. This third band is not constant; in other similar solutions from grass I failed to see it. The two first bands read: λ 490·5 to λ 470; 2nd, λ 458·5 to λ 445 (?). On treating the solid residue from this solution with iodine in iodide of potassium it became green, with nitric acid dirty green, and with sulphuric acid green and slaty-blue. A chloroformic solution of the yellow residue showed three distinct bands, two of which read: 1st, λ 501 to λ 481; 2nd, λ 467 to λ 451 (?). A bisulphide of carbon solution showed only two distinct bands: 1st, λ 521·5 to λ 498·5; 2nd, λ 488 to λ 470.

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* Compare spectrum 1, Chart I., with spectra 1 and 7, Chart II., and it is seen that the bands of the solutions giving the latter spectra are nothing more than those found in a living leaf. I am quite certain about the presence of a band between D and E in a living leaf.

† The yellow residue also gave the reactions described by HANSEN with iodine, nitric, and sulphuric acids.

An attempt to obtain the needle-shaped crystals of chlorophyll yellow only partially succeeded.

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* It is a remarkable fact that the decomposability of vegetable chlorophyll differs very much in different cases. I often failed to bring about this change with caustic soda in similar solutions, which also causes precipitation in such solutions. *Cf.* DRAGENDORFF's "Plant Analysis," 2nd Eng. ed., 1884, p. 114, note; here it is shown that possibly the chlorophyll may exist in different states of combination in plants.

† Possibly two bands may have been formed; note the above readings; this appearance also varies very much in different cases. I frequently noticed a narrow dark band placed over a lighter one.

‡ The diminution of the fluorescence by alkalies appears to be due to precipitation.

On then agitating the soap with ether alone, this took up some colouring matter, becoming green and showing a fine red fluorescence. The first alcohol-ether extract did not take up much "chlorophyll green," but the second was a fine green colour with a red fluorescence; this would teach that the apparent loss of fluorescence on treating an alcohol solution of chlorophyll with caustic soda is merely due to precipitation, otherwise the persistence of fluorescence after saponifying cannot be accounted for. The bands of this solution now, however, were totally different in position from those of the original solution, as was always found to be the case; thus they read: 1st, λ 649 to λ 627; 2nd, λ 600 to λ 582 (?); 3rd, λ 540 to λ 524·5, they are shown in spectrum 11, Chart II. I would also call attention to spectrum 12, Chart II., which is that of a shallow depth of this solution. The band far over in violet is not a lipochrome band, for if it were the other bands should be present; it read from λ 468 to λ 451. (Dr. SORBY[*] shows a similar band in the spectrum of blue chlorophyll.) Its presence in similar solutions is, however, not constant.

The solution of saponified chlorophyll, from which the petroleum-ether and the ether had removed the above pigments, showed also a changed spectrum, its bands now reading: 1st, λ 649 to λ 620·5; 2nd, λ 602·5 to λ 582.

To see the exact change which had taken place by saponification an ether-alcohol solution was evaporated down and the residue dissolved in absolute alcohol; a green solution was thus obtained showing spectrum 13, Chart II., of which the bands read: 1st, λ 669 to λ 649; 2nd, λ 640 to λ 627; 3rd, λ 613 to λ 593; 4th, uncertain; and on comparing these measurements with those of the bands of the first absolute alcohol solution a great discrepancy is apparent. Moreover, the results of saponifying grass chlorophyll do not exactly coincide with those obtained by saponifying that of *Primula*, but even in the case of grass *the results are not by any means constant.* Whether this is due to the fact that chlorophyll varies in composition according to season remains to be proved, but the following observations show that such discrepancies may occur.

A solution obtained by digesting grass in ether, to which rectified spirit had been added, gave a series of bands agreeing closely with those seen in the above absolute alcohol solution. They read: 1st, λ 679·5 to λ 640; 2nd, λ 629 to λ 598; 3rd, λ 591 to λ 566; and 4th (about), λ 548·5 to λ 532. In a thin layer: 5th, λ 486·5 to λ 467; and 6th, λ 451 to λ 438. On saponifying and extracting as described above with petroleum-ether, the resulting yellow solution showed only *two, not three,* bands: the first, λ 490·5 to λ 472; and 2nd, λ 458·5 to λ 445 (examined by daylight). The ether extract showed only one feeble band in red, but the ether and alcohol extract gave spectrum 14, Chart II., the bands reading: 1st, λ 669 to λ 654; 2nd, λ 640 to λ 627; 4th, λ 543 to λ 532; and 5th, λ 511·5 to λ 492·5. The mother liquid gave practically the same bands. This discrepancy is not of great importance, as spectra 13 and 14 really belong to the same pigment, but spectra

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[*] Proc. Roy. Soc., vol. 21 (1873), pp. 442 *et seq.* Compare SACHSSE, "Die Chemie und Physiologie der Farbstoffe," &c., S. 24, &c.

14 and 11 do not agree (spectrum 14 represents probably a pigment more changed than spectrum 11).

The above experiments are sufficient to show that the chlorophyll of plants is altered by saponification, but I have now to show that it is not altered in the same manner nor to the same extent as *Spongilla* chlorophyll and enterochlorophyll.* At times I found the same *splitting up* of the dominant band by caustic soda, but the bands did not give the same readings as in a similar solution of *Spongilla* chlorophyll.

Thus taking an alcohol solution of grass chlorophyll, whose bands read as follows: 1st, λ 683·5 to λ 640; 2nd, λ 627 to λ 600; 3rd, λ 593 to λ 566; 4th, λ 551 to λ 535; and saponifying as before, I found that the ether-alcohol extract gave a double band in red, the first one very narrow and faint, the second darker, and a band in violet *not* due to the yellow chlorophyll constituent. These read (approximately): 1st, λ 669 to λ 660; 2nd, λ 649 to λ 631; and the one in violet λ 460 to λ 443·5 (?); in a deeper layer, however, other bands were seen, and one broad band in red covered the space occupied by the first two seen in a thin layer, the whole series reading: 1st, λ 672 to λ 623; 2nd, λ 609 to λ 580·5; 3rd, λ 540 to λ 527; 4th, (about) λ 511·5 to 494·5.

The ether solution also gave the double band in red, while only one could be seen in the mother solution (soap-lees), namely, the second of the two bands in red.†

Now in this case I used only enough caustic soda to ensure the saponification of the fat, so that the splitting up of the band in red was not due to an excess of alkali.

The grass was obtained in spring, and the leaves were young, which probably accounts for the results obtained.

Saponification of the Chlorophyll of Spongilla lacustris.—Spongilla may be taken as a typical example of an animal which builds up chlorophyll. The observations of Prof. RAY LANKESTER‡ and SORBY§ have shown this beyond doubt; hence it is most suitable for deciding the question which I had to answer. Does animal chlorophyll contain the same green and yellow constituents as vegetable chlorophyll, and is it similarly affected by saponification?

I have been able to examine the chlorophyll of *Spongilla* in great abundance, as I had a good deal of material upon which to work. The spectrum yielded by the living sponge is shown in spectrum 2, Chart I. If portions of this sponge are digested for some time with ether containing alcohol, and the extraction repeated as long as the solution becomes green, a fine green solution is obtained, showing a blood-red fluoresce[illegible] and in a deep layer giving spectrum 15, Chart II., of which the bands read: 1s[illegible] 678 to λ 640; 2nd, λ 627 to λ 600; 3rd, λ 589 to λ 566; 4th, λ 548·5 to λ 529·5; wh[illegible] are practically the same as the bands of a similar solution of plant chlorophyll. On evaporating such a solution, and dissolving the residue in absolute alcohol, a similar spectrum is obtained, of which the bands read: 1st, λ 678 to λ 647, and a shading to λ 640; 2nd, λ 625 to λ 598; 3rd, λ 591 to λ 569; 4th, λ 548·5 to λ 532; and also a lipochrome band beginning at λ 494·5 and extending to λ 468, also probably a second which could not be measured.

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* Saponification does not always affect the dominant band in red to the same extent. Professor FOSTER, in looking over some of my preparations, noticed that in one case the centre of the bands, before and after saponifying, was the same; hence the decomposability of chlorophyll differs in different cases. See above, which was written before this foot-note.

† The petroleum-ether extract of the soap from this chlorophyll showed only *two* bands when examined by sunlight, their positions corresponding to those already given.

‡ Quart. Journ. Micro. Soc., *loc. cit.*

§ *Ibid.*, vol. 15, N.S., p. 47.

That this pigment should be changed by saponification appeared likely, *à priori*, from the action of caustic soda on an alcoholic solution, which was not the same as in the case of plant chlorophyll. On adding this reagent two bands appeared in the red at first of equal intensity, the first band being the original chlorophyll band, the other when it first appears being much less shaded; the latter then gets darker, and all the bands finally appear as shown in spectrum 16, Chart II. The action of nitric acid is similar to its action on enterochlorophyll and plant chlorophyll, the solution becoming bluish eventually, and giving these bands: 1st, λ 669* to λ 638; 2nd, λ 613 to λ 591; 3rd, λ 577·5 to λ 558·5; 4th, λ 543 to λ 521·5, and 5th, about λ 505 to λ 484·5. The most noticeable change with acetic acid was the marked intensification of the 4th band from the red, but it is not correct to say that a *new* band appeared with acetic acid, *it had been already there and became intensified.*

An absolute alcohol solution of this chlorophyll was saponified by Hansen's method. The petroleum-ether solution (after saponification) was yellow and gave two bands in the violet half of the spectrum, but also two bands in the red in a deep layer. Spectrum 17, Chart II., is the result of combining a deep and shallow layer. The presence of the bands in red may be due to the saponifying not having been thoroughly carried out.† The other bands read: 1st, λ 490·5 to λ 468; 2nd, λ 458·5 to λ 445. *In the second petroleum-ether extract the green constituent was also present.* The yellow constituent could not be made to crystallize distinctly. It became in the solid state greenish with iodine in iodide of potassium, a well-marked blue and blue-green with sulphuric acid (also a violet and brown tint appeared for a short time), and green with nitric acid. Hence it gave the same reactions as the yellow constituent of plant chlorophyll.

The ether extraction removed nearly all the green colouring matter from the soap; it was green and did not show a very distinct fluorescence. Its spectrum is shown in spectrum 18, Chart II., and its bands read: 1st, λ 669 to λ 658·5; 2nd, λ 649 to λ 636; 3rd, λ 613 to λ 589; 4th, λ 576 to λ 560; 5th, λ 545·5 to λ 529·5; and 6th, about λ 513 to λ 496·5 (?). After this extraction the soap-lees was, as usual, agitated with ether containing alcohol, but, contrary to what I found in the case of

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[*] The shifting of the band in red not being as well marked as in other cases.

[†] Although in this and other cases I followed Hansen's directions exactly.

plant chlorophyll, the latter solution was almost colourless, the previous ether extraction having taken up the green colouring matter. The "chlorophyll green" was obtained from the ether extract on evaporation in the form of spherical crystals giving a black cross with crossed NICOLS. The mother liquid from which the above extracts had been removed also showed a double band in red and a feeble shading before D, so that it contained the same pigment as that present in the ether extract. Hence it is quite evident that *Spongilla* contains a colouring matter which in alcoholic solution gives the same spectrum as vegetable chlorophyll; it further resembles the latter in being composed of a green and a yellow constituent, but its behaviour with caustic soda in the cold, and on saponification with it, shows that it is decomposed into a body whose spectrum is not the same as that of a solution of vegetable chlorophyll similarly treated. The green constituent, and probably the yellow, are however crystallizable in the same forms as the constituents of vegetable chlorophyll.

Saponification of Enterochlorophyll.[*]—To obtain a sufficient supply of enterochlorophyll for saponification from the *oyster*, twenty "livers" were removed and repeatedly extracted with absolute alcohol as long as they gave up anything to it. The united extracts furnished an olive-yellow solution with a blood-red fluorescence, the solution giving almost the same bands as a similar solution of leaf green as regards the red half of the spectrum, but wanting that after D. Thus such a solution gives spectrum 1, Chart III. and 2, III. in a thinner layer. The bands read: 1st, λ 672 to λ 654, shading up to λ 640; 2nd, λ 620·5 to λ 595; 3rd, λ 545·5 to λ 532; the 4th band about λ 501 to λ 475. On saponifying and shaking with petroleum-ether the green constituent—or, at least, what answers to it in this case—was taken up with the yellow one, and the solution gave two bands in red, as shown in spectrum 3, Chart III.; and in a thin layer one band appeared, as shown in spectrum 4, Chart III., in the blue and green from about λ 505 to λ 475. In the hope of separating the green from the yellow constituent this solution was evaporated down and again extracted with petroleum ether, but again the band in red was seen. On filtering a petroleum-ether solution an orange stain was left on the paper. Hence the lipochrome present in the enterochlorophyll (in this case) of *Ostrœa* differs from that of *Spongilla* and plant chlorophyll in giving only one band. *It resembles* KÜHNE'S *rhodophan or xanthophan, while in Spongilla and in plants the lipochrome is more like chlorophan.*[†]

On extracting the soap with ether this became a yellow-green colour, and showed a faint band in red and abrupt absorption of the violent end of the spectrum.

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[*] It seems highly probable that the individual differences found by me on saponifying enterochlorophyll are due simply to the fact that it is present in various stages of formation, presenting a parallel in this respect to plant chlorophyll.

[†] According to KÜHNE, *loc. cit.*, chlorophan gives two bands, rhodophan, a very broad dark shading, absorbing the spectrum from D onwards towards violet, and recalling to mind tetronerythrin, *which I am inclined to think it is*, and xanthophan one band.

The alcohol-ether extract of the soap was yellowish-green and did not show a marked fluorescence; it showed a band in red and another evidently due to the presence of a lipochrome. On evaporating it down and extracting the residue with absolute alcohol a solution was obtained, giving spectrum 5, Chart III., the band in red reading λ 675 to λ 657.

The mother liquid also gave two bands in red, spectrum 6, Chart III., and the other faint bands shown in that spectrum. The first read λ 669 to λ 654, and second λ 638 to λ 623.

The residue from a petroleum-ether extract did not give a distinct colour change with iodine in iodide of potassium, it became green with nitric acid, and a less distinct green with sulphuric acid. In other cases the greenish colour with iodine was better marked.

The occurrence of the one-banded lipochrome in the enterochlorophyll of *Ostræa* is the rule, as other experiments taught, and it is very difficult to separate it from the green constituent; still, although a complete separation of the yellow from the green constituent cannot be easily accomplished by saponification, it is quite evident that the enterochlorophyll of *Ostræa* is composed of these constituents, and bears a most remarkable resemblance to plant chlorophyll and to that of *Spongilla*, differing slightly in the fact that it is more decomposed by saponifying than either and in a different manner.*

I saponified an alcohol extract of the liver of *Helix pomatia* by the same method. Just as in the case of *Ostræa* and *Spongilla* the green constituent went into the petroleum-ether, giving a band in red from λ 672 to λ 657, also a lipochrome band from λ 503 to λ 482·5, and the other solutions only contained decomposition-products of the green constituent mixed with the yellow. This enterochlorophyll was much changed by the saponification, and, like that of *Ostræa*, contained a one-banded lipochrome.

The remaining experiments on the saponification of enterochlorophyll were carried out on that of starfishes and *Mytilus*, and owing to greater abundance of material gave more satisfactory results. Taking an absolute alcohol extract, giving the spectrum described under specimens (4) and (5), *supra*, and saponifying it, and then extracting the soap with various solvents, I found that the petroleum-ether only gave *one* lipochrome band between green and blue, and no bands in red. The ether solution, however, showed perhaps one band λ 490·5 to λ 470,† and no band in red. In chloroform the yellow residue—left on evaporating the ether—formed a deep yellow solution showing only *one* band, λ 505 to λ 481, and in deeper layer general absorption of the violet and blue, thus resembling KÜHNE's rhodophan or xanthophan. On evaporating the chloroform an orange-coloured residue was left, and on touching this with a solution of iodine in iodide of potassium it became perhaps redder, with nitric acid bluish and then green, with sulphuric acid a blue, blue-green, and in parts brownish colour.

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* Although there was only one lipochrome band in the above extracts, yet in some cases the fatty matter coloured by the chlorophyll, which separates out on evaporating an alcohol solution, gave two bands belonging to the lipochrome.

† Perhaps another from about λ 456·5 to λ 443·5.

The ether-alcohol solution was yellowish, showing a band in red in a deep layer, and absorption of the blue and violet parts of the spectrum, and now all the other bands of the chlorophyll spectrum had disappeared, as shown in spectrum 7, Chart III. Hence the enterochlorophyll had become changed by saponifying; it contained a yellow and a green constituent, the former a one-banded lipochrome as in the case of *Ostræa*.

A solution (alcohol), giving the spectrum described under (7), from the radial cœca of several specimens of *Uraster* was saponified as before. The petroleum-ether extract of the soap showed only *one* band, spectrum 8, Chart III., from λ 488 to λ 475, and in a chloroform extract of the residue from λ 516 to λ 484·5. The ether solution also showed the same band from λ 494·5 to λ 475, and no other.

The ether-alcohol solution was yellowish, and showed one band in red and strong absorption of the blue and violet (and one lipochrome band*).

The mother liquid (after removal of these extracts) gave a double band in red, the first λ 669 to λ 651·5, and second λ 636 to λ 623, and as the original solution showed only *one* band in red, it is quite evident that the enterochlorophyll had become changed by saponifying.

A solution (alcoholic) from the cœca of (13) and (14) was saponified as before. The yellow petroleum-ether extract gave *two* lipochrome bands, the first from λ 498·5 to λ 473·5, and the second λ 458·5 to λ 445, and no band in red.†

The ether solution of the soap was greenish-yellow, and left the soap green; it also contained the lipochrome constituent. The alcohol-ether extract was greenish, and on concentration showed a band in red, spectrum 9, Chart III., and as before only one band in red is seen, showing how the green constituent had been altered.

The mother liquid (soap-lees) gave two bands in red as before, the first λ 665 to λ 649, and second λ 636 to λ 623.

On evaporating a petroleum-ether solution distinct yellow needles, such as HANSEN describes, were obtained (see Plate 10, fig. 7), and the residue also gave a slate-blue and green with sulphuric acid, a green with nitric acid, and it became slightly reddish with iodine in iodide of potassium. The alcohol-ether solution also on evaporation left crystals, some of which occurred as minute round green granules, and larger spherical crystals showing a fine black cross with crossed NICOLS. I have also sketched these in the drawing (Plate 10, fig. 8), they are evidently the same as those obtained by HANSEN from vegetable chlorophyll. I also saponified the enterochlorophyll of

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* Even the band in red is only seen in a deep layer. The lipochrome band is not shown in the map.

† It is worthy of notice that complete separation is accomplished in this case, when there is a double lipochrome band.

Mytilus edulis, using for the purpose the alcohol extracts of twenty-eight "livers." The bands of the solutions so obtained *were not affected* by treatment with caustic soda* in the cold, nor on boiling with it. Their readings were as follows: 1st, λ 683·5 to λ 649; 2nd, λ 623 to λ 596·5; 3rd, λ 547 to λ 535; the bands nearer the violet, of which there were two, could not be measured.

On saponifying as before, I found that the separation of the green from the yellow constituent could not be completely brought about, the petroleum-ether giving a band in red from λ 675 to λ 657. Two lipochrome bands were also barely visible, which could not be measured; moreover, the first ether extract removed all the colouring matter from the soap, as in the case of *Spongilla*. This solution was a dull yellow-green colour, and its bands were but little different from those of the original chlorophyll solution; they read: 1st, λ 683·5 to λ 649; 2nd, λ 640 to λ 629; 3rd, λ 620·5 to λ 596·5; 4th, λ 543 to λ 532, and two others belonging to the yellow constituent too faint to be measured. The mother liquid (soap-lees) gave a band in red, λ 675 to λ 651·5, and another, λ 640 to λ 625. It will be noticed that the most important change was the appearance of the λ 640 to λ 629 band—which was very faint—in the ether solution.

On attempting to extract the yellow constituent from the green by evaporating the ether solution, and extracting with petroleum-ether, I failed, as both constituents were dissolved by it. This result was so constant that I think it may be accepted as a peculiarity of enterochlorophyll.

The "chlorophyll-yellow" in this case gave, in the solid state, a yellow colour with iodine in iodide of potassium, a green and blue with sulphuric acid, and a transient blue with nitric acid. Hence it is a lipochrome.

The enterochlorophyll of *Mytilus*, obtained by evaporating an alcohol solution, is insoluble in water, soluble in alcohol, ether, chloroform, bisulphide of carbon, benzol, petroleum-ether, and in *olive oil*. Its solubility in the last medium explains how it is held in solution in oil drops in many cases.

It is coloured, in the solid state, a fine blue-green and green with strong sulphuric acid, which does not destroy the bands, as they are seen in the resulting green solution after filtering through asbestos, but not in the same position as before. They are the same bands as those seen in a solution of enterochlorophyll after treatment with nitric acid. Nitric acid colours the solid pigment blue-green, which eventually disappears, and is replaced by a red colour. Hence by saponifying it is clear that enterochlorophyll differs from plant chlorophyll with regard (1) to the difficulty of separating its green from its yellow constituent; (2) to the position of the bands in a petroleum-ether extract of the yellow constituent; (3) in the fact that while this yellow constituent gives a similar colour reaction with nitric and sulphuric acids, it gives a different colour with iodine in iodide of potassium in most cases.

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* A similar effect was noticed in the case of *Ostræa*, the solution becoming more orange after boiling with NaHO.

Absence of Starch and Cellulose, and Morphology of Enterochlorophyll.

In none of the above cases was chlorofucin found; and I have shown in my paper "On the Chromatology of Actiniæ" it ought to be present if symbiotic algæ are present, and in animals living on marine algæ it ought to be present if the "liver" chlorophyll be due to intracellular digestion of food chlorophyll. It was also necessary to see whether starch and cellulose were present, and to attempt to study the morphology of the pigment. The results strikingly confirm the spectroscopic evidence and support the idea that enterochlorophyll is built up by the animal.

I found the best results were obtained by freezing the "livers" and examining the frozen sections. For this purpose the small ether-freezing microtome of CATHCART answers admirably. The freezing method has to be adopted since if the tissues are hardened in alcohol the chlorophyll is removed; and alcohol would be required because other hardening agents alter the pigment. The relationship of the enterochlorophyll to the gland cells is, however, difficult to make out in frozen sections, but I think it is found in all cases within the epithelium cells lining the "liver" tubes.

I made various sections of invertebrate "livers" obtained from animals feeding and fasting, but never obtained a trace of starch or cellulose with iodine in iodide of potassium, SCHULZE'S fluid, or with iodine and sulphuric acid. These experiments were made on the "livers" of *Helix aspersa, Anodonta cygnea, Patella vulgata, Ostræa edulis, Mytilus edulis, Astacus fluviatilis,* the cœca of starfishes, &c. The precautions recommended by GEDDES:[*] of previously digesting the tissues in alcohol, and in caustic potash, and neutralising with acetic acid, having been adopted in each case. Now, if food-products were present we ought to get starch or at least cellulose; and if symbiotic algæ were present the product of their activity, starch, and the cellulose wall of the alga itself, should be present; but they are not; hence these tests alone furnish a strong argument in favour of the purely animal origin of enterochlorophyll.

A section of the "liver" of *Ostræa edulis* under a low power such as a 1-inch or 2-inch shows tubes cut in different planes, oblique, transverse and longitudinal, and the pigment appears to be distributed mainly along the periphery[†] of the tubes, the centre of each tube in cross-section contrasting strongly with the periphery, the former being colourless, the latter deeply coloured. The pigment appeared in the form of fine granules, some yellow, some brown, and others of intermediate tints. The granules are not all round, some being angular. In teased-out specimens the pigment seemed disposed in bands along the long diameter of each tube, and in cross-sections of the tubes a section of four such bands forming a kind of cross can be seen. Besides occurring in granules, singly and in aggregates, some of which are round, the pigment is also dissolved in oil globules and may be present in the diffused condition. No unicellular algæ can be seen.* (See Plate 10, fig. 2.)

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[*] "Nature and Functions of the 'Yellow Cells' of Radiolarians and Cœlenterates." Proc. Roy. Soc., Edinburgh, vol. 11 (1882), p. 377.

[†] Not the extreme periphery is meant, but that portion between the centre and the wall of the tube, *i.e.* the secreting part. This is only seen in cross-sections. In teased-out specimens almost the whole tube appears coloured.

In *Uraster* the smaller cœcal tubes are seen packed with oil globules of a yellow colour, some of which are very large, and this appearance is so constant that I think one would be correct in assuming that here the enterochlorophyll is mainly dissolved in oil.

In *Patella*, sections show the tubes of the "liver" cut in various planes, the pigment occurring mostly in very fine granules of a yellow colour, and as in *Ostræa* it is distributed along the periphery † of the tubes, sometimes in the diffused state. Some yellow oil globules are also seen. The granular pigment appears to be confined to the epithelium cells lining the tubes.

In *Littorina*, the "liver" itself has the same kind of structure, but so little connective tissue holding the tubes together, that the sections readily fall to pieces. The enterochlorophyll occurs in very small granules, of an orange colour, in small round cells, and in oil globules, some of which have a greenish tint. On the whole, it appears confined to the periphery of the tubes. (See Plate 10, fig. 1.)

In *Purpura lapillus*, the amount of pigment is very small, and of a pale-yellow colour; the epithelium lining the periphery of the tubes seems to contain the pigment mostly in a diffused condition.

In *Limnæus stagnalis* the enterochlorophyll occurs in round and angular minute granules, also in oil globules, some of which are yellow, others a more pronounced green. Coloured cells of an epithelial type, some of which enclose granules, and others diffusely stained with the colouring matter, are also found. These latter are doubtless the epithelial lining cells of the "liver" tubes. (Plate 10, fig. 4.)

In *Helix pomatia* the enterochlorophyll is found in granules and oil globules; also in peculiar cells probably of an epithelial type, some of which contain granular pigment, and others are diffusely stained of a green and yellow-green colour. The latter probably belonging to the lining of the cell spaces of the "liver."‡

In *Helix aspersa*§ the appearances are much the same, but the large round brown bodies are very peculiar (see Plate 10, fig. 5). It would seem that the latter are coloured by the hæmatin constituent of the "bile"; the enterochlorophyll occurs in the periphery of the cell spaces and in their epithelial lining. The large brown cells measured from 13 μ in diameter to 15 μ, other yellowish-brown cells from about 8 μ to 4 μ, down to $1\frac{1}{3}$ μ. There are green oil globules $8\frac{1}{2}$ μ in diameter, some $5\frac{1}{2}$ μ of a yellow colour, others are coloured by a mixture of yellow, green, and brown, measuring 4 μ and some 2 μ. The brown bodies do not lose their colour when extracted with alcohol, while the yellow and green constituents do. In none could I find a trace of starch or cellalose. Here also the enterochlorophyll occurs in granules. In hibernating snails there are an immense number of coloured oil globules in the "liver," as well as granular pigment.

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* In *Mytilus edulis* the pigment occurs very richly in round brownish-yellow granules, also in small oil globules.

† *I.e.*, in the secreting cells.

‡ In the "bile" certain spherical crystalline bodies are seen which I hope to examine shortly.

§ I am rather inclined to the belief that in *Helix* and *Limax* after feeding some food chlorophyll is taken up into the "liver."

In *Limax* there are large green cells stained uniformly (of a pale-green colour), these cells measure from 17 μ to 13 μ, down to 10 μ, some being larger and some smaller, which are probably the "liver" cells. There are not so many coloured oil globules, but abundance of pigment in minute granules. The latter can be seen enclosed in the cells (secreting epithelium) lining the cell spaces.

In none of the cells could starch or cellulose be detected, nor were any unicellular algæ present.

On the whole, then, it would appear that enterochlorophyll occurs dissolved in oil globules, also in the granular form, and sometimes dissolved in the protoplasm of the secreting cells of the "liver." *In no case can unicellular algæ be found.*

Remarks.

This investigation, although not as complete as I had hoped to make it, yet, I believe, decides the question as to the animal origin of enterochlorophyll, and also shows that in *Spongilla* a true animal chlorophyll is built up.

What I call chlorophyll in this paper is the mixture of colouring matters which can be extracted from the green leaves of land plants by means of alcohol, or alcohol and ether, and the spectrum consists of the six bands described, whose wave-lengths are given above. These bands, except one, are the bands seen in a living leaf, concerning which Sachs[*] remarks, after adducing the evidence of Gerland and Rauwenhoff,[†] "It is not easy to understand how certain physicists can maintain the contrary." Vogel is however cited by Dragendorff[‡] in support of the statement[§] that "in examining a fresh leaf only the most marked line between B and C is seen." But his statement is sufficiently refuted by the drawings of the spectra which accompany this paper, compare, *e.g.*, spectrum 1, Chart I., with spectra 1, 2, 7, 8, of Chart II. The colouring matters present in an alcohol solution are (in those cases where I have examined such a solution), at least two, a green and a yellow. The former giving four bands, the latter generally two. No doubt can exist as to the truth of this statement in the mind of any one who carefully studies the literature[||] of chlorophyll and then makes the experiments recorded in this paper.

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[*] 'Botany,' 2nd Eng. ed., p. 758.

[†] 'Archives néerlandaises,' vol. 6 (1871), p. 604; also 'Poggendorff's Annalen,' band 143 (1871), p. 585.

[‡] 'Plant Analysis,' Eng. ed., 1884, p. 19.

[§] 'Berichte der deutschen Chemischen Gesellschaft,' band 11 (1878), pp. 623 and 1367.

[||] See also Askenasy, Bot. Zeit., 1867, p. 225; Kromayer und Ludwig, Archiv d. Pharm., band 156 (1861), p. 164; Aé, do., band 192 (1870), p. 163; Wiesner, Chem. Centralblatt, 1874, p. 353; Filhol, 'Comptes Rendus,' tome 61 (1865), p. 371; Hartsen, Annalen der Phys., band 146 (1872), p. 158; Sachsse, Chem. Centralblatt, 1878, p. 121, also 'Die Chemie und Physiolologie der Farbstoffe,' &c., 1877.

Professor **Stokes**,[*] **Fremy**,[†] **Sorby**,[‡] **Kraus**,[§] and latterly **Hansen**[||] and others may all be quoted as authorities in support of the view that plant chlorophyll is composed of more than one constituent. **Pringsheim** maintains that **Fremy**'s view : namely that the constituents exist side by side in chlorophyll, is erroneous, and holds that they are only products of decomposition.[¶] Which of these views is right it is impossible to say with our present knowledge. Still we know that chlorophyll consists of two or more constituents united together in some way.

Spongilla contains a similar chlorophyll, and this is built up by the animal itself, a comparison of the measurements in this paper, and of spectra 1, 7, and 15, Chart II., proves this beyond all doubt. In Cantharides[**] an animal chlorophyll also exists, but I have not saponified it; and in all the chlorophyll-containing animals enumerated in **Sachs**'s 'Botany,' by Professor **Lankester**, with one or two exceptions, *e.g.*, *Idotea* and *Bonellia*, I have no doubt a similar chlorophyll exists. In *Anthea cereus* it is due to symbiotic algæ.

A comparison of the bands of enterochlorophyll as they are shown in Chart I., with those of vegetable chlorophyll in Chart II., shows a difference with regard to the bands in the violet half of the spectrum, and on running the eye down along the F line one sees that the bands belonging to the yellow constituent are joined in some cases, in others placed close together, and in some cases only one band is present, which replaces the other two. After saponifying the same result is arrived at. The yellow constituent of the enterochlorophyll, while generally giving in the solid state the colour reactions of **Schwalbe** and **Capranica**, shows different bands to those of vegetable "chlorophyll yellow" (=xanthophyll).

I do not think that **Hansen**'s "chlorophyll green" is a body which exists *as such* in chlorophyll, because the examination of its solutions after saponification reveals a wide difference in the position of the bands of the "chlorophyll green," compared with those belonging to the red half of the spectrum in the original chlorophyll solution. What its relationship may be to the greenish-white body crystallizing in four-sided plates, and appearing red by transmitted light, which **Hoppe-Seyler**[††] isolated from grass, is doubtful, or what to the other substance isolated by him crystallizing in needles, dark green by reflected and brown by transmitted light, and named *chloro-*

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[*] Proc. Roy. Soc., vol. 13 (1863–4), p. 144. **Burnett**, "Lectures on Light," 2nd course, pp. 8 and 9.

[†] 'Comptes Rendus,' tome 50 (1860), p. 405; tome 61 (1865), p. 180. Journ. für prakt. Chem., band 87 (1862), p. 319.

[‡] *Loc. cit.*

[§] *Loc. cit.*

[||] *Loc. cit.*

[¶] Chem. Centralblatt, 1880, pp. 299, 316, 331; also **Konrad**, 'Flora,' 1872, p. 396.

[**] See Brit. Assoc. Reports, 1883. I have recently examined again a solution obtained by digesting the *elytræ only* in ether containing alcohol and find that chlorophyll is present.

[††] 'Berichte der deutschen Chemischen Gesellschaft,' Jahrg. 12 (1879), p. 1555; Jahrg. 13 (1880), p. 1244.

phyllan, is equally doubtful. The former substance is, according to **Dragendorff**,[*] probably the same as **Bougarel's**[†] *erythrophyll*. **Gautier's**[‡] crystalline body is, according to **Hoppe-Seyler**, a mixture of erythrophyll, chlorophyllan, and wax.

Still **Hansen's** method is useful because it enables one to see if the chlorophyll of animals can be made to yield the same constituents as that of plants, and if the solutions yield the same spectra after saponifying.

It is unnecessary to repeat the account of the results I obtained, but I may say that it appears that vegetable chlorophyll is considerably changed by saponification, so is *Spongilla* chlorophyll, and so is enterochlorophyll. A likeness in all the spectra of the solutions of these chlorophylls is, however, apparent after saponifying, and the *ultimate* constituents crystallize in the same form, so far as I can judge from **Hansen's** description. The mere fact that it is most difficult to separate the saponified constituents of animal chlorophyll from each other, while it is easy enough in the case of vegetable chlorophyll, goes to show that the constitution of the respective chlorophylls differs, and this fact, taken in connexion with the microscopic, spectroscopic, and chemical evidence, seems to me to establish almost beyond doubt that in the case of enterochlorophyll we are dealing with an animal product.

I have not quoted nearly all the papers written on chlorophyll, as this would be a great and unnecessary task.[§] The following table giving the wave-lengths of the bands in solutions of enterochlorophyll, *Spongilla* chlorophyll, and plant chlorophyll, shows at a glance the agreements and differences between them :—

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[*] *Loc. cit.*, p. 115.

[†] Bulletin de la Soc. Chim., tome 27 (1879), p. 442.

[‡] *Ibid.*, tome 28 (1879), p. 147.

[§] **Russell** and **Lapraik** (Journal of Chem. Soc., vol. xli., p. 338) describe a splitting up of the dominant band of chlorophyll into two by caustic alkalies, and cite **Chautard** ('Comptes Rendus,' tome 76., p. 570), in support of this statement. They also state that on heating chlorophyll with solid potash it is completely decomposed, the dominant band disappearing. **Hansen** insists on the avoidance of too much caustic alkali, and in all cases I tried to follow his directions as closely as possible. See also paper in Journal of Chem. Soc., by **Tschirch**, 1884, p. 57; and **Pringsheim's** "Researches on Chlorophyll," by Professor B. **Balfour**, Quart. Journ. Micr. Soc., vol. 22, p. 75, &c. In **Sachsse's** treatise, *loc. cit.*, a great number of authorities are quoted.

COMPARISON of Enterochlorophyll, Chlorophyll of Grass and Spongilla.

Band.	Paludina. Rectified Spirit.	Limnæus. Rectified Spirit.	Trochus Z. Absolute Alcohol.	Trochus C. Rectified Spirit.	Littorina. Absolute Alcohol.	Patella. Absolute Alcohol.	Grass. Absolute Alcohol.	Spongilla. Absolute Alcohol.
I.	λ λ 678 to 656	λ λ 678 to 651·5	λ λ 672 to 651·5	λ λ 678 to 657	λ λ 678 to 654	λ λ 678 to 654	λ λ 679·5 to 636	λ λ 678 to 640
II.	620 to 600	618 to 600	618 to 593 (?)	620·5 to 595	623 to 600	620·5 to 598	627 to 600	625 to 598
III.	0 Uncertain	0 "	0 "	0 "	0 "	0 "	593 to 566	591 to 569
IV.	552 539	547 to 537	548·5 to 535	545·5 to 535	548·5 to 537	547 to 536	551 to 532	548·5 to 532
V.	?	519 to 503	?	519 ——	496·5 ——	521·5 ——	486·5 to 467	494·5 468
VI.	?	492·5 473·5	?	—— 484·5	—— 477 (with NaHO)	—— 475	451 438	?

REMARKS.

On allowing for the difficulty of measuring the edges of feeble bands, the errors of refraction caused by varying temperatures of room and difference of solvent, a tolerably close agreement is apparent with regard to the bands (I.–IV.) in the red half of the spectrum. Those in the violet half differ much, not only between enterochlorophyll and grass chlorophyll, but between the latter and *Spongilla* chlorophyll, which is in agreement with the result of saponifying. The third chlorophyll band is generally missing from the spectrum of enterochlorophyll, but the position of the other bands teaches that it is not a decomposition-product of chlorophyll. Especial stress should be laid on the λλ of band in red, especially on the wave-length of its redward edge; this being the most deeply shaded *is the last to disappear* on dilution.*

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* Prof. STOKES suggested that by adopting the "fractional" method of separation I might have more easily arrived at the same results. Accordingly this was done, when it was found that the constituents of enterochlorophyll could be *partially* separated from each other. But the behaviour of enterochlorophyll is not the same as that of plant chlorophyll under these conditions, as the green constituent goes into the spirit, and the yellow into the bisulphide, which proves that the pigments are dissolved in a medium differing from that which holds them in solution in the plant.—(July 24, 1886.)

EXPLANATION OF PLATE 9.

CHART I.

Sp. 1. Spectrum of a living leaf of common grass and of the other leaves mentioned in this paper. The fourth band is exaggerated.

Sp. 2. A bit of *Spongilla* examined in the same way.

Sp. 3. Spectrum of an *Ophrydium.*

Sp. 4. Enterochlorophyll of *Paludina vivipera* in rectified spirit.

Sp. 5. Enterochlorophyll of *Limnæus stagnalis* in absolute alcohol.

Sp. 6. The same solution treated with nitric acid.

Sp. 7. Enterochlorophyll of *Trochus ziziphinus* in absolute alcohol.

Sp. 8. Enterochlorophyll of *Trochus cinerarius* in alcohol.

Sp. 9. Enterochlorophyll of *Littorina littorea* in absolute alcohol.

Sp. 10. Spectrum of the "liver" of *Littorina littorea* examined with an achromatic substage condenser and SWAN lamp.

Sp. 11. Enterochlorophyll of *Patella vulgata* in absolute alcohol.

Sp. 12. "Bile" of *Patella vulgata* showing enterohæmatin.

Sp. 13. Diluted alcohol solution of the "liver" of *Helix pomatia.*

Sp. 14. A second absolute alcohol extract of the same "liver."

Sp. 15. Absolute alcohol extract of the "liver" of another *Helix pomatia.*

Sp. 16. Enterochlorophyll of *Solaster papposa* in rectified spirit.

Sp. 17. Enterochlorophyll of *Uraster rubens* in alcohol.

Sp. 18. Enterochlorophyll of another specimen of *Uraster rubens* in absolute alcohol, showing the double band in red.

Sp. 19. The solution giving spectrum 18 was evaporated to dryness, and the residue extracted with petroleum-ether gave this spectrum. (*Cf. Spongilla*-chlorophyll.*) The second band in red is a shade too broad.

CHART II.

Sp. 1. Chlorophyll of *Primula* in absolute alcohol, deep layer.

Sp. 2. The same, shallow depth, showing the bands of "chlorophyll yellow" at F and before G.

Sp. 3. Petroleum-ether solution of the "chlorophyll yellow" of *Primula* after saponifying.

Sp. 4. The mother liquid, after separation of the ether, alcohol ether, and petroleum-ether extracts, showing how the chlorophyll bands have been displaced by the saponification.

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* Some of these spectra represent the result of examining a deep and shallow layer of liquid.

Sp. 5. The second ether-alcohol extract of the soap from *Primula*; compare with spectrum 1. All the bands are displaced.

Sp. 6. Alcohol solution of the same "chlorophyll green" (after saponifying) with nitric acid; early stage of reaction.

Sp. 7. Absolute alcohol solution of chlorophyll of common grass.

Sp. 8. The same, thin layer of liquid. These bands really agree with those of spectrum 2; (see measurements).

Sp. 9. Action of caustic soda in the cold on an alcohol solution.

Sp. 10. Petroleum-ether extract of the soap from this chlorophyll, showing a three-banded "chlorophyll yellow" spectrum (=xanthophyll).

Sp. 11. Second alcohol-ether extract of the same soap, showing changed position of the bands of "chlorophyll green." (*Cf.* spectrum 7.)

Sp. 12. Shallow depth of same solution. Note the band between F and G.

Sp. 13. Alcohol solution of the saponified "chlorophyll green," obtained as described in the paper.

Sp. 14. Ether-alcohol extract of saponified chlorophyll from common grass in another experiment.

Sp. 15. Alcohol-ether extract of chlorophyll of *Spongilla* before saponifying.

Sp. 16. The action of caustic soda in the cold on an alcohol solution of the same.

Sp. 17. Petroleum-ether extract of the same after saponifying.

Sp. 18. Ether extract of the same soap, showing complete change in the spectrum caused by saponifying.

CHART III.

Sp. 1. An absolute alcohol solution obtained from the "livers" of 20 specimens of *Ostræa edulis.*

Sp. 2. The same thinner layer showing only one band in the violet half of the spectrum.

Sp. 3. The above solution after concentration by evaporating was saponified, and the petroleum-ether extract of the soap gave this spectrum, showing that the constituents, both that corresponding to the "chlorophyll green" in other cases and that corresponding to the "chlorophyll yellow," are taken up by this solvent.

Sp. 4. The spectrum of a thinner layer of the same.

Sp. 5. Ether-alcohol extract of the same soap evaporated, and the residue dissolved in alcohol.

Sp. 6. The mother liquid (soap-lees) after extraction with these solvents, showing how the original spectrum has become completely changed.

Sp. 7. Alcohol-ether extract obtained from the saponified enterochlorophyll of *Uraster rubens.* All the bands, except that in red, have disappeared, and even this is only visible in deep layers.

Sp. 8. Petroleum-ether extract of this saponified enterochlorophyll showing only one band.

Sp. 9. Alcohol-ether extract obtained as described under spectrum 7 in another experiment.

The measurement of bands in the microspectroscope from which all the above spectra were mapped is attended with greater difficulty than in the chemical spectroscope owing to the shortness of the spectrum; hence some trifling errors of position may creep into the maps, which for that reason are not as reliable as the measurements given in this paper, each of which has been worked out by an interpolation curve from the readings of the photographed scale of the large chemical spectroscope. The remarkable agreement in these measurements—all of which were worked out independently of each other—shows that the wave-length method is the most reliable one, combined with the use of a spectroscope of moderate dispersion.

EXPLANATION OF PLATE 10.

In Plate 10, I have endeavoured to show the appearances presented by enterochlorophyll when fresh frozen sections of the "livers" of Invertebrates are examined under a power of about 320 diameters. The drawings do not show the *relative proportions* of the constituent cells, granules, &c., but merely the most typical appearances in each case. To save printing in too many colours, the latter have been made more uniform than they actually appear in the specimens.

Fig. 1. Enterochlorophyll of *Littorina littorea*, principally in granules and dissolved in oil globules.

Fig. 2. Ditto, from "liver" of *Ostræa edulis* in the same form, the liver cells containing the pigment.

Fig. 3. Ditto, from "liver" of *Helix pomatia*, the larger cells containing granules are probably the secreting cells, whose protoplasm is stained with the pigment, and some of which contain larger granules than others.

Fig. 4. Enterochlorophyll of *Limnæus stagnalis*, in granules, oil globules, and secreting cells of "liver," some of which have their protoplasm diffusely stained with the pigment, and contain the latter also often in granules.

Fig. 5. Ditto, from "liver" of *Helix aspersa*, the transition from green to brown and the presence of the large brown spherical bodies is very remarkable. Very few "liver" cells are here shown.

Fig. 6. Ditto, from "liver" of *Limax*. The large epithelial liver cells are uniformly stained with the pigment, besides containing it in the granular form; in other cases oil globules containing the pigment are seen.

Fig. 7. Crystals (which, according to HANSEN, are those of the lipochrome*) from a petroleum-ether extract of saponified enterochlorophyll of *Uraster rubens* (the outline of lower figure is that of a droplet of liquid).

Fig. 8. Crystals obtained from an alcohol-ether extract of the same soap (belonging, according to HANSEN, to "chlorophyll green").

Fig. 9. The same with crossed NICOL'S, but without selenite, showing the peculiar black cross.

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* It has yet to be proved whether these crystals may be merely coloured by the lipochrome; possibly (?) they belong to one of the fatty acids, *cf. e.g.*, crystals of the so-called margarin.

VI. *Researches on Myohæmatin and the Histohæmatins.*

By C. A. MacMunn, *M.A., M.D.*

Communicated by Professor M. Foster, *Sec. R.S.*

Received October 19,—Read November 26, 1885.

[Plates 11, 12.]

In a short paper read before the Physiological Society* in 1884 I gave a preliminary account of a new colouring matter which I had discovered in muscle by means of the spectroscope; also of a class of colouring matters found in the tissues and organs of invertebrate and vertebrate animals to which the former pigment evidently belongs, and which I named histohæmatins from their occurrence in the animal tissues. The name myohæmatin was proposed for the muscle pigment for reasons which will be given further on.

Since the publication of that paper I have been engaged in working out the distribution of these pigments in the Animal Kingdom, and have tried to find out their relationship to other colouring matters and the changes produced in them by reagents.

Methods of Investigation.—These colouring matters have been missed by other observers owing to their not having adopted the methods of examination used by me. The portion of tissue or organ under consideration is examined in a "compressorium," by means of which any required thickness can be examined; it is illuminated by a strong light condensed upon it by means of a substage achromatic condenser, and is examined by a spectrum eye-piece in a binocular microscope. The advantage of using a binocular instrument consists in this:—That one of the tubes is used as a finder, and in enabling one to see what is furnishing the spectrum. A one-inch objective is the most suitable power for this purpose, though sometimes the ⅛th or ¼th may be required. The objectives have been shortened and the condenser so arranged as to allow of the full illumination of both fields when the ¼th and ⅛th objectives are used. A Swan lamp was sometimes used, sometimes direct sunlight, but in many cases a good Argand gas-burner is sufficient. Observations were frequently checked (and measurements made in wave-lengths) by bringing the object in the compressorium before the slit of a large one-prism chemical spectroscope,† and I have latterly derived great assistance by the use of an instrument provided with shutters in the eye-piece by means of which any portion of the spectrum can be cut off, which was made by ADAM HILGER. When an object is examined in the chemical spectroscope it has to be illuminated by a bull's-eye condenser placed between it and the light-source.

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* Proc. Physiol. Soc., 1884, No. IV., December 13.

† Although all the following measurements were made with the same instrument, and are, therefore, valuable for comparison, *inter se*, yet, owing to the great difficulty of seeing these bands, they may require slight modifications by and by.

Animals Examined.—My observations have been confined necessarily to such animals as can be procured in an inland place, but the number examined is sufficient to prove the wide distribution and importance of the pigments to be described. Had my opportunities been greater the results would doubtless have been more important.

Among invertebrates various mollusca, echinoderms, arthropods, and some worms have been examined; the results of the examination of actiniæ have been already communicated to the Royal Society. Among vertebrates various reptiles, amphibians, fishes, birds, and mammals have been examined, and the results obtained show that there is no essential difference in the spectra of the organs and tissues of vertebrates and invertebrates, when the influence of the circulating hæmoglobin in the former has been eliminated.

I. THE HISTOHÆMATINS.

In Dr. SORBY's paper on the "Evolution of Hæmoglobin"* a remark occurs which shows that he had seen a spectrum which is that of a histohæmatin. Speaking of the hæmatin first observed by him in the bile of *Helix* he says:—"I think it very probably does occur in the muscles of the foot and elsewhere," &c. Here at least a previous observer—whose opinion is of great weight owing to his skill in chromatology—suspected the existence of a hæmatin-like pigment in the tissues of an animal, and believed it to be related to the hæmatin of the bile of the same animal. Not only, however, does a histohæmatin occur in an animal whose "bile" shows a hæmochromogen-like spectrum, but also in other animals in which no hæmochromogen can be detected in the "bile," and the bands of the respective histohæmatins are absolutely identical. Moreover we find the histohæmatin spectrum replaced by that of a hæmochromogen-like spectrum in the solid organs and tissues in individual cases; it is for that reason that I have named these pigments histohæmatins. No other observers, so far as I know—except Dr. SORBY and myself—have seen, or at least have recorded, the occurrence of such a spectrum in the organs or tissues of an animal.

Histohæmatins of Echinodermata.

The tissues and organs of various echinoderms have been examined, and in most of them the appearances differ in no respect from those seen in *Uraster rubens.* In this species the spectra are well marked, and may be taken as typical, their bands being very sharp and easily seen.

If we compare the spectrum of the generative organs of *Uraster* with that of muscle, or with that of the blood-free pancreas of a cat, a most striking resemblance is apparent. Such a statement may appear startling but is nevertheless true, as I have convinced myself by repeated examination and measurements. The eggs of most animals when examined by this method show the lutein band or bands, but in *Uraster* the spectrum is entirely different and belongs to a typical histohæmatin.[*] We find a narrow band before D, two still narrower between D and E, and two others faint nearer the violet, spectrum 1, Chart I. They gave the following readings (approximately):—

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* Quart. Journ. Micros. Soc., vol. XVI., New Series, pp. 77 *et seq.*

1st band . . .	λ 613	to	λ 591, or 593,	
2nd band . . .	λ 569	„	λ 560,	
3rd band . . .	λ 556	„	λ 548·5,	
4th band . . .	λ 537	„	λ 516	(about).

A great number of specimens were examined and in all the same spectrum observed.

The stomach-wall likewise gave a distinct spectrum which bears a close resemblance to hæmochromogen, spectrum 2, Chart I. The first of these bands read λ 566 to λ 558·5 (approximate). There is evidence to show that elsewhere in this species a histohæmatin occurs; thus the spectrum of the ampullæ resembles that of the stomach-wall.

I tried by various solvents to isolate these pigments but failed. The colour of the organs in which they occur is a more or less pale-yellow. The bands appear to become darker on treatment with reducing agents, and less shaded on exposure to the air, although the change from the oxidised to the reduced state is not easily brought about.

In the integument of *Uraster rubens*, when it has a brownish tint, the presence of hæmatoporphyrin[†] can be easily proved, and as the only pigments present in the animal are enterochlorophyll in the radial cœca, histohæmatins in the tissues, and a lipochrome here and there, and as hæmatoporphyrin cannot be obtained from enterochlorophyll or from the lipochromes, it is highly probable it is a metabolite of the histohæmatins; or what is less likely that these pigments may be derived from the same radical.

In *Ophiactis virens*, M. FŒTTINGER[‡] states that he found hæmoglobin, but KRUKENBERG[§] thinks this observation incorrect, and that the water-vascular system of this echinoderm probably contains a pigment related to the bile-hæmatin ("helico-rubin" of KRUKENBERG, my enterohæmatin) of *Helix*. I was inclined at first to agree with KRUKENBERG for the reasons given above.[*]

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[*] A small quantity of a lutein (=lipochrome) can be got out of the eggs by absolute alcohol. The male generative organs contain histohæmatin as well as the eggs.

[†] It occurs in the integument in the condition of hæmatoporphyrin as such, as can easily be proved by examining the scraped-off pigment with the microspectroscope. I first showed its presence in this situation. Proc. Birm. Phil. Soc., vol. iii., p. 378. It can be isolated by digesting the integument in alcohol and sulphuric acid. Journ. Physiol. vol. vii., pp. 240–252.

[‡] Bull. Belgian Acad., No. 5.

[§] "Grundzüge einer vergleichenden Physiologie der Farbstoffe," &c., p. 134.

Histohæmatins of Mollusca.

In this sub-kingdom one meets with appearances which prove the great importance of the histohæmatins from a physiological point of view, and prove their connexion with, and replacement by, pigments which are known to be connected with hæmoglobin and its derivatives. SORBY'S remarks on the presence of certain bands in the foot of *Helix* have been given above.

Littorina littorea.—Hæmoglobin occurs in the pharyngeal muscle,[†] and I have changed it into hæmatin, both acid and alkaline, it here *occupies the place of myohæmatin* as a comparison with other species shows.

In the yellower parts of the foot two faint bands like those of hæmochromogen can be detected. In other fleshy parts of the body we get a spectrum which resembles myohæmatin, if we suppose the second and third band of its spectrum to have coalesced (spectrum 3, Chart I.).

Purpura lapillus.—Hæmoglobin occurs in the pharyngeal muscle replacing the myohæmatin of other species.

In the foot, a histohæmatin spectrum is visible, resembling that of *Littorina* (spectrum 4, Chart I.). In other parts of the animal no bands are with certainty visible, except in the liver (referred to in former papers), but here and there a faint histohæmatin spectrum can be just seen.

Trochus cinerarius.—The pharyngeal muscle contains hæmoglobin. Contrary to what I found in *Littorina*, it is absent from the radula. Faint traces of a histohæmatin are present, but none distinct enough to map.

Patella vulgata.—Hæmoglobin occurs in the pharyngeal muscle, and in the radula in traces. The foot shows a distinct histohæmatin spectrum, and in other parts faint traces of its bands are just visible.

In most specimens these bands resembled closely those of hæmochromogen, and, since the latter is present in its "bile," as I have shown, there can hardly be a doubt that this pigment is taken up from the intestine and deposited in the tissues as a histohæmatin.

In *Limnæus stagnalis* and *Paludina vivipara*, besides the hæmoglobin in the pharyngeal muscles, there is evidence elsewhere of the presence of a histohæmatin, but the examination of these species is yet incomplete.

In *Mytilus edulis*, in the mantle, a distinct histohæmatin spectrum is apparent, and on comparing this with the spectrum of myohæmatin and with other histohæmatins a very striking likeness is apparent.[‡] In the ovaries a somewhat similar spectrum is seen, differing from that of the mantle in this that the two second bands are fused into one. (See Chart I., spectra 5 and 6.) In the heart there is an attempt at a myohæmatin spectrum. In the gills, and in the adductor and retractor muscles, faint bands may be seen in some specimens belonging to the histohæmatins.

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[*] HOWELL has, however, recently found hæmoglobin in a *Holothurian*, which tends to support FŒTTINGER'S statement. June 16, 1886.—JOHNS HOPKINS University Circular, v., 1885.

[†] And in the radula. In the liver of some I have detected bands like those of hæmochromogen.

[‡] After STOKES'S fluid the bands read:—1st λ 613–596·5; 2nd, λ 569–563; 3rd, λ 556–550.

In *Ostræa edulis* the fleshy abdomen gives a distinct, though faint, histohæmatin spectrum :—a faint band before D, and another in green like the first band of hæmochromogen. On treatment with sulphide of ammonium the spectrum is better defined. On examining two or three thicknesses of mantle placed over each other a similar spectrum is seen. A similar pigment occurs in the gills, only that the band before D is invisible. In the stomach wall, intestine, and in the adductor muscle we meet with similar appearances. It requires a practised eye to recognise these bands with certainty.

In other lamellibranchiate mollusca, such as *Unio* and *Anodonta*, histohæmatins occur especially in the foot, but it is in the pulmonate mollusca that their spectra are most distinct. Just as in birds and in insects, where respiratory activity is greatest, we find the myohæmatin spectrum best marked, so in the air-breathing mollusca the histohæmatins are better marked than in other members of their sub-kingdom. It is worthy of notice that in *Helix*, *Limax*, *Arion*, and others the "bile" contains enterohæmatin, and that in *Limax* and *Arion*, just as in *Uraster rubens*, the integument can be made to yield hæmatoporphyrin as I have shown.* I think here, too, there can be little doubt that the histohæmatins are the mother substance of the integumental hæmatoporphyrin. In the heart of all the pulmonate mollusca and in their buccal muscles myohæmatin occurs, as will be shown further on.

In *Helix aspersa* (besides the heart and pharyngeal muscle) spectra are perceptible in the *dartsac*, in the *ovo-testis, vas deferens, albumen gland* in the *foot*, in the wall of *crop*, in the *receptaculum seminis*, in the *oviduct*, in the *penis*, in the *nephridium*, and in the *finger-shaped gland* (CLAUS). In most of these a faint band before D occurs, and either one broad band occupying the position of the second and third myohæmatin bands, or one or two faint bands resembling and placed nearly in the position of those of hæmochromogen. The spectra correspond so closely with those seen in *Limax* that those figured for *Limax* will illustrate the above.

In the *receptaculum seminis* of one *Helix* a redder portion was visible, which showed spectrum 7, Chart I., and which is remarkable for its likeness to methæmoglobin. In the *nephridium* the spectrum was well marked, and either showed a feeble band before D and a broader and darker one between D and E, spectrum 8, Chart I. (from *Limax*), or two narrow bands in green closely resembling the second and third of myohæmatin (spectrum 9, Chart I.).

In *Helix pomatia* similar spectra can be observed. In the foot a band, or sometimes two, corresponding to those of hæmochromogen, are visible ; a similar spectrum in the *dartsac*, and similar spectra in the same parts as those in *Helix aspersa*. *Limax* shows similar spectra. In the heart and pharyngeal muscles myohæmatin occurs; in the *nephridium* spectrum 8, Chart I., is seen; in the *ovo-testis* a faint band before D and a narrow one in green like the first of hæmochromogen; in the albumen gland a similar spectrum (spectrum 10, Chart I.); and the *vas deferens* gave spectrum 11, Chart I., resembling that of the *foot* closely. All specimens of *Limax maximus L. flavus* and *L. variegatus* presented similar appearances.

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* Proc. Birm. Phil. Soc., *loc. cit.*, and Journ. of Physiology, vol. vi., p. 38 ; vol. vii., pp. 240–252.

In *Arion ater* the *nephridium* showed a spectrum resembling that of myohæmatin (*cf.* spectrum 9, Chart I.), while the spectra of its other organs are the same as those in *Limax*. The spectrum of the nephridium is remarkable for its resemblance to that of the kidney of vertebrates.

Histohæmatins of Arthropoda.

In this sub-kingdom the histohæmatins are the same as those already described; they are well marked in the crustacea, of which *Homarus vulgaris, Cancer pagurus, Carcinus mænas, Astacus fluviatilis* and *Pagurus bernhardus* have been examined. In the hearts of all these I have found myohæmatin, which will be referred to further on. Among *Arachnida* I have examined *Epeira diadema,*[*] *Tegenaria civilis* and other spiders in which myohæmatin occurs, but owing to the smallness of their parts the occurrence of other histohæmatins although very probable is not quite certain. In *Insecta* we meet with *myohæmatin* in abundance, but owing to the thinness of the intestine and the small size of the *ovaries, malpighian tubes,* &c., one cannot be certain as to the presence of the histohæmatins. There are, however, exceptions to this statement, which will be referred to again.

Astacus fluviatilis.—In this species enterohæmatin is found in the bile, as already described by me,[†] myohæmatin in the heart, but apparently not in the voluntary muscles.

In the yellow *stomach-wall,* after washing well with water, the spectrum in some cases shows that figured in spectrum 12, Chart I. This is remarkably like that seen in the nephridium of *Arion* and in the kidney of higher animals (vertebrates). In other specimens this spectrum is replaced by another in which the narrow band in green is like that found in *Uraster,* but this, from what has been already shown, is merely a modification of the other (spectrum 13). In the green gland (nephridium) of all the specimens examined the same spectrum is seen, and is shown in Chart I., spectrum 14. The branchiæ sometimes show a hæmochromogen-like spectrum (spectrum 15, Chart I.). The ovaries only gave a lutein-like spectrum.

In *Homarus vulgaris* one finds myohæmatin present in the muscle of the heart, but apparently absent in the voluntary muscles. The *stomach-wall* shows a faint band before D, and another faint and narrow one in green similar to those seen in the same situation in the crayfish. The *green-gland* gives the same spectrum as that of the latter species also (spectrum 16, Chart I.). In the *vas deferens* and the *branchiæ* no bands could be detected.

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[*] The livers of these spiders show a distinct band before D and a darker one in the green, therefore a histohæmatin spectrum; *cf. Carcinus.*

[†] Proc. Roy. Soc., vol. 35, p. 381.

In *Cancer pagurus* and *Carcinus mœnas* similar spectra* were observed. In *Pagurus bernhardus*, whose heart muscle contains myohæmatin, there are faint traces of histohæmatins, but not distinct enough to map their spectra.

Among *Insecta*, as already stated, the presence of histohæmatins is difficult to determine. In the crop and other parts of the enteron faint bands coincident with those of histohæmatin may be seen in some species; one might expect to meet with myohæmatin in this situation owing to the muscle of the intestine being striped in insects, but hitherto I have not found it. In the mouth parts of some larvæ myohæmatin occurs (*e.g.* Ennomos), and, as will be shown again, all adult insects possess myohæmatin in their voluntary muscles.

In *Staphylinus olens* we meet with a most remarkable spectrum, yielded by the testes, which shows that the hæmoglobin-forming tendency is not altogether suppressed in insects. I have not met with this appearance in other species.

In the specimens of *Staphylinus* examined the testes were a fine carmine colour; squeezed out in the compressorium, and examined in the usual manner, they gave two bands possessing a remarkable resemblance to those of reduced hæmatin (spectrum 17, Chart I.). Before squeezing down the cover-glass of the compressorium the spectrum resembled oxyhæmoglobin, but in a suitable thickness the bands appeared as shown. It will be noticed the first band is placed over a shading which occupies nearly the position of the band of reduced hæmoglobin. The position of these bands is approximately: 1st, λ 569 to λ 554·5, and 2nd, λ 540 to λ 524·5. I succeeded in converting this pigment into acid hæmatin by the action of acetic acid, by which the bright red colour was changed to a dull brown and the spectrum into that of acid hæmatin. As spermatozoa were easily seen in these organs with the microscope there can be no doubt as to their nature.

Vermes.

In *Lumbricus*† and *Hirudo* all the organs which in other species show histohæmatin spectra appear to contain a small amount of hæmoglobin, which doubtless functions in a similar manner to the histohæmatins.

In *Aphrodite*, besides the hæmoglobin contained in the ventral chain of ganglia, I have detected traces in the muscular fore-gut.

Histohæmatins in Vertebrata.

In *Vertebrata* the search for histohæmatins in the organs and tissues is attended with difficulty, owing to the presence of hæmoglobin, but fortunately the bands of the histohæmatins can be recognised in the tissues or organs when squeezed out to a degree of thinness which no longer allows the bands of hæmoglobin to be seen, and in most cases the blood-vessels can be injected with salt solution sufficiently to eliminate the influence of the circulating hæmoglobin.

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* The *liver* of *Carcinus mœnas* shows a band before D and a dark one in green.

† *Lumbricus* contains hæmatoporphyrin in the dorsal streak. For *Serpula* and *Sabella* see my paper "On the Chromatology of the Blood of some Invertebrates," Quart. Journ. Micros. Science., vol. C., p. 469.

Although Birds and Mammals present the best marked histohæmatin spectra, yet to preserve the continuity of this paper *Fishes* will be dealt with first. I will, however, deal briefly with this class, as the spectra of their organs are not as well marked as in other classes. In the golden carp (*Cyprinus*), the mackerel (*Scomber scombrus*), the herring (*Clupea heringus*), the roach (*Leuciscus rutilus*), and the tench (*Tinca vulgaris*), the stomach-wall, liver, kidney, and intestinal wall, and perhaps other organs, present histohæmatin spectra. In some the spectra are obscured by the presence of oxyhæmoglobin, which appears sometimes to replace them.

The spectrum yielded by the liver and kidney is that shown in spectrum 1, Chart II.* In some parts of the kidney the band shown there is apparently replaced by two resembling in this point the spectrum of the kidney in other animals.

In other fishes similar spectra were observed, and in every species examined I found myohæmatin.

Amphibians.

In *Rana temporaria* a well-marked histohæmatin spectrum can be seen in the *stomach-wall*, spectrum 2, Chart II. The *testis* appears to contain traces of the same bands. The *liver* shows a band covering D, and a darker between D and E. In the *spleen*, besides that of reduced hæmoglobin a similar spectrum occurs, also in the *kidney*.

In *Bufo vulgaris* the same organs show similar spectra.

In *Hyla arborea* there are traces of similar spectra, but they are much obscured by the presence of oxyhæmoglobin. The spectrum of the kidney is worthy of notice.

In *Salamandra maculosa* the histohæmatin spectra in the kidney, liver, stomach-wall, and spleen are much obscured by the presence of hæmoglobin, but there is distinct evidence of their presence.

The Mexican Axolotl (*Siredon pisciformis*) presents well-marked spectra belonging to this class. Thus the liver shows a faint band at D, and another faint one between D and E, besides a third nearer violet, spectrum 3, Chart II. In the cortex of the kidney a well-marked histohæmatin spectrum (spectrum 4, Chart II.), which recalls myohæmatin to mind. In the stomach-wall another even more closely resembling that of myohæmatin, and in the intestine a similar spectrum (spectrum 5, Chart II.).

In the so-called red frog (species ?) the appearances are similar, the kidney showing the same double band between D and E as in Axolotl, &c. In the liver and spleen a histohæmatin spectrum like that of *Rana* occurs. The stomach-wall shows a similar spectrum to that of the kidney, especially after immersion in weak reducing agents, such as water, to which a few drops of sulphide of ammonium have been added.

In all these Amphibians myohæmatin is found.

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* From the tench.

Reptiles.

In *Tropidonotus natrix* the liver, spleen, kidney, and wall of intestine show the histohæmatin bands. In the testis they also appear to be present. In a small black snake (species ? probably *Bascanium constrictor*) the liver and kidney showed histohæmatin spectra, but in the stomach-wall and intestine only traces of oxyhæmoglobin could be made out.

A small mud turtle, belonging to the genus *Trionyx*, showed in its liver, spleen, and especially in the kidney (spectrum 6, Chart II.), the usual histohæmatin spectra. In the stomach-wall only oxyhæmoglobin could be seen. In *Emys Europea* the liver and spleen showed a faint band at D, and another between D and E exactly resembling those of other animals. In the kidney a double band, as in the last case, was just visible. In the stomach-wall and that of the intestine the bands were remarkably distinct and resemble those of myohæmatin (spectrum 7, Chart II.). I found that if the portions of these organs, *e.g.*, spleen, liver, stomach, and intestine were steeped in STOKES's fluid, the bands of the histohæmatin spectrum became much better marked. On exposure to air they became fainter; hence the banded spectrum belongs to the reduced state, and the bandless to the oxidized, and this was found to be the rule in other cases.*

In *Lacerta viridis* these spectra are beautifully marked, especially in the stomach-wall and kidney, the sharpness of the bands being much increased by steeping in glycerin. In the cortex of the kidney there is a band before D, and one, or more generally two, occupying the position of the single band, and placed closely together between D and E (spectrum 8, Chart II.). In the stomach-wall the spectrum closely imitates that of myohæmatin (spectrum 9, Chart II.), and in the intestine a somewhat similar spectrum is seen. In both these parts marked intensification of the bands is produced by dipping them into ammonium sulphide diluted with water. In the liver the spectrum is remarkable for the presence of a darker band than usual at the blue end of green in addition to those of a histohæmatin (spectrum 10, Chart II.).

In *Lacerta agilis* the same spectra are seen, also in *Scincus officinalis*.

In all the above Reptiles myohæmatin has been found.

Birds.

The common rock pigeon, *Columba livia*, furnishes evidence of the presence of histohæmatins, differing in no way from those already described. In the spleen, pancreas, liver, and kidney, the bands are well marked, especially in the last (spectrum 11, Chart II.). In the liver I have also detected free hæmochromogen. The gizzard appears mainly, if not altogether, coloured by hæmoglobin, at the same time the second oxyhæmoglobin band appeared much too dark, and was therefore probably intensified by the presence of another band belonging to a histohæmatin.*

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* Another point about the histohæmatin spectra is that they become much more distinct after the organ or tissue has been steeped in glycerin for some hours. I think this is probably due to shrinkage and the consequently greater condensation of the pigments in a given space, and to the clearing action of the glycerin.

These spectra are better marked in the snowy owl (*Nictea nivea*); in this species the cortical and medullary portions of the kidney give a beautifully-marked histohæmatin spectrum (spectrum 12, Chart II.). The liver and spleen furnish the same spectra seen in other species :—a feeble band at D, and a darker between D and E.

The stomach-wall contains oxyhæmoglobin mainly, and this result is interesting when compared with the result of examining the gizzard of other birds.

The pancreas contains a histohæmatin. In the lung oxyhæmoglobin only could be detected, and this was the case in all vertebrates examined, although not previously mentioned.

At the suggestion of Professor MOSELEY I examined the gizzards of several birds, and found generally only oxyhæmoglobin ; but in many cases I noticed the darkening of its second band as referred to above.

Other birds, *e.g.*, fowls, swifts, sparrows, and owls were examined, with results the same as the above.

Mammals.

I place the greatest reliance on the results of the examination of the organs and tissues of Mammals, because I have been better able to eliminate the influence of hæmoglobin in them by injecting the blood-vessels thoroughly with salt solution; and in the quite bloodless organs the histohæmatin spectra are well marked.†

I do not think it necessary to figure the spectra observed in each species of mammal examined, because they are all the same practically for each organ and tissue ; but describe as briefly as possible the result of the examination of each species.

In the *hedgehog* we find histohæmatin spectra in the liver, spleen, kidney, and stomach-wall, which are the same as those found in the species already described. They may also be present in other organs, but I was satisfied at finding them in those referred to.

The *guinea pig* presents well-marked spectra belonging to the same class, in the liver in which the band between D and E is very dark, probably due to the presence of free hæmochromogen; in the spleen, in which treatment with ammonia causes the spectrum of hæmochromogen to appear, and in the kidney, where, as in the hedgehog, a double band occurs between D and E and a feeble band at D (spectrum 13, Chart II.). In the stomach-wall I only observed the bands of oxyhæmoglobin.

In the *supra renal capsule* the *medulla* shows the bands of hæmochromogen well marked, in fact its first band is *black*. In the cortex the spectrum is mainly that of oxyhæmoglobin, while the intermediate zone gives the spectrum of a histohæmatin. These spectra are figured in spectrum 14 and spectrum 15, Chart II. The significance of these spectra will be referred to again.

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* See below.

† The same method was partially successful in removing the influence of hæmoglobin in Fishes, Reptiles, and Amphibians.

In the *rat* (especially after injection of the blood-vessels with salt solution) well-marked histohæmatin spectra can be seen. The kidney (spectrum 16, Chart II.) is remarkable for the resemblance of its spectrum to that of myohæmatin, the liver shows a feeble band at D, and a darker one between D and E, the pancreas a similar spectrum to that of the cat's pancreas, the spleen, a spectrum like that of the liver, and the stomach-wall a beautifully defined spectrum, closely resembling that of the kidney (spectrum 17, Chart II.). In the wall of the intestine similar bands occur, and the adrenals show a well-marked hæmochromogen spectrum, *which is not as distinct after injection with salt solution as it is when no injection has been used.*

The *rabbit* is a suitable animal for the demonstration of these spectra. In the spleen the spectrum observed was the same as before; the liver was remarkable for its hæmochromogen-like spectrum (spectrum 1, Chart III.); and this spectrum was got from lobules which were quite free from blood. In the kidney, the band between D and E was single, and occupied approximately the position of the double band usually observed there, and was seen in both cortical and medullary parts; in other cases spectrum 3, Chart III., was seen. The adrenals gave the spectrum of hæmochromogen in the medulla, and that of a histohæmatin in the cortex (see spectrum 2, Chart III.).

In the *dog* the spectra are similar, the spleen, liver, and kidney, stomach-wall, and supra-renal body having been examined. The medulla of the adrenals showed the hæmochromogen bands, but not as distinctly as in the guinea pig and rabbit. I was unable to measure the bands of these spectra with sufficient accuracy for wave-length calculation until I had examined the blood-free organs of the cat.

In the *cat* one can see the edges of bands by bringing the portions of organ or tissue, after thoroughly injecting with salt solution, under examination before the slit of a chemical one-prism spectroscope, as they are very distinct. Thus for the stomach-wall the following measurements were made (see spectrum 4, Chart III.)—the organs being blood-free:—

1st band (before D) λ 613 to λ 593,
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 551.

A similar spectrum is yielded by the pancreas, of which the first band extends from:—

λ 613 to λ 596·5,

and the others read:—

2nd band . . . λ 569 to λ 563,
3rd band . . . λ 556 „ λ 548·5,
4th band . . . λ 532 „ λ 513 (?).

(Chart III., spectrum 5.)

In the liver the bands read :—

1st band . . . λ 613 to λ 596·5,
2nd band . . . λ 569 „ λ 548·5,
3rd band . . . λ 537 „ λ 521·5 (?).

(Chart III., spectrum 6.)

It is worthy of notice that the second band exactly occupies the place of the second and third bands of the histohæmatin spectrum of the pancreas.

A similar spectrum is yielded by the kidney (cortex) in which the bands read :—

1st band . . . λ 613 to λ 596·5, or λ 593,
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550. (Chart III., spectrum 7.)

In the wall of the small intestine the bands are exactly the same as in that of the stomach.

In the ovary there is also a peculiar spectrum, which is like that of hæmochromogen, but the bands are much fainter than those of the medulla of the adrenals. (Spectrum 8, Chart III.)

The adrenals, after injection with salt solution, do not show the hæmochromogen spectrum nearly as distinctly as in a cat whose blood-vessels are not thus treated. This observation obviously proves that a portion of the hæmochromogen has been washed out by the injection, and that, therefore, it must be looked upon as an excretion. (See Chart III., spectrum 9.)

Comparing now the measurements of the above spectra in wave-lengths with those of myohæmatin, one cannot help concluding that these spectra belong to the same class of pigments, or indeed to the same pigment; hence these observations prove that *myohæmatin belongs to the histohæmatins;* and had my vision been more acute, I believe I could have proved the same thing for the histohæmatin spectra of all the animals examined.

Having now proved the point which has been foreshadowed by previous observations, I may refer to some other observations as briefly as possible.

Histohæmatins have been found in the mesenteric lymphatics of the *pig*, and in the kidney, liver, and spleen of the same animal, and hæmochromogen in its adrenals; in the liver, kidney, spleen, and mesenteric glands of the *ox* and *sheep* and hæmochromogen in their adrenals.

In *man* I failed to find a histohæmatin spectrum in the thyroid, the spectrum being that of oxyhæmoglobin; the same remark applies to the pituitary body. In the thymus of a child, aged 10 months, I perceived a faint histohæmatin spectrum, but not in its thyroid. In the spleen, liver, and kidney of man, the spectra are the same as in other Mammals, and in the human adrenals hæmochromogen can be detected in the medullary part, while the cortex furnishes evidence of the presence of a histohæmatin. To be quite certain as to the exact spectra of the histohæmatins in man, injection of the blood-vessels with salt solution would be required, and until this has been done I do not feel warranted in drawing conclusions from other observations which I have made on the human organs. In man, however, the presence of myohæmatin has been detected, as will be described further on, as well as its occurrence in the other Mammals referred to above.

In nervous tissues* I have not yet found a histohæmatin, either in invertebrates or vertebrates.

In no animal have I succeeded as yet in isolating the histohæmatins. In them the coloured constituent occurs united to a proteid in all probability, and hence the difficulty attending attempts at isolation. Bisulphide of carbon, chloroform, alcohol, ether, benzol, petroleum, hot and cold water, alkaline water, acidulated water, and other solvents have been tried in vain.

On the other hand, oxidation and reduction can be brought about in the *solid* organs and tissues. An interesting point bearing upon this is that the bands of the spectrum of the histohæmatin in the stomach of the rat are invisible if the animal be killed during digestion, but bits of the stomach-wall plunged into a reducing agent, show in a short time the banded spectrum; the reason of this is that the histohæmatin is charged with oxygen during digestion as denoted by its bandless condition. At all events, I have proved to my own satisfaction that the *banded condition belongs to the reduced state, and the bandless to the oxidised;* but it would appear from what I have to relate about myohæmatin that this oxidation and reduction are not as simple as the reduction and oxidation of hæmoglobin, for example, the oxygen being apparently more firmly fixed than in the case of oxyhæmoglobin.

Thus, from Echinoderms† to man throughout the animal kingdom, we find in various tissues and organs a class of pigments whose spectra show a most remarkable resemblance to each other; they are allied to hæmochromogen, the bands of which are sometimes closely imitated by the histohæmatins. They are probably simpler in constitution than hæmochromogen prepared from vertebrate blood, at least they do not yield all its decomposition products; their bands are intensified by alkalies and enfeebled by acids, intensified by reducing agents, and enfeebled by oxidising agents; they accordingly appear to be capable of oxidation and reduction and are therefore *respiratory.* If this view be correct, and I have every reason to believe that it is, we may consider that the histohæmatins are of use in enabling the tissues in which they occur to take up the oxygen from the circulating blood and *hold it* in the tissues, exchanging for it the carbon dioxide. Hence the histohæmatins are concerned in the *internal* respiration of the tissues and organs of invertebrate and vertebrate animals. Why a

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* The occurrence of hæmoglobin in the ventral chain of ganglia of *Aphrodite* (LANKESTER) is worthy of notice.

† The pigments of *Actiniæ* which replace (in them) the histohæmatins have been described in my paper on the "Chromatology of Actiniæ," Phil. Trans., vol. 176, p. 641.

coloured constituent should be more useful than a *colourless* one is not clear, but in hæmoglobin, hæmocyanin, and my echinochrome and Professor LANKESTER's chlorocruorin, as well as probably in SORBY's aphidein, we have colouring matters which are *respiratory pigments*.

II. MYOHÆMATIN.

Until I had discovered the colouring matter which I have named myohæmatin, it was believed by all physiologists that hæmoglobin was the colouring matter to which the voluntary and cardiac muscles of animals owe their colour. The diaphragm of the rabbit after injection with salt solution being the muscle which has been used to demonstrate the presence of hæmoglobin (KÜHNE[*]). While there is no doubt about the presence of hæmoglobin in the plasma of the muscle of the heart, and in that of the voluntary muscles of most vertebrates, as KÜHNE and others have shown, or in the muscular fibres of certain gasteropod molluscs, as Professor LANKESTER has shown, there is convincing evidence of the presence of myohæmatin in the cardiac and voluntary muscles of invertebrates and vertebrates, which myohæmatin either accompanies, replaces, or is replaced by hæmoglobin in individual cases. I will now give an account of the observations by which I have been led to this conclusion. I may, however, state here that Professor KÜHNE has informed me that he has long "suspected" the presence of a yellow colouring matter in muscle.[†]

Myohæmatin in Arthropods.

It is now about two and a half years since I discovered a new spectrum in the muscles of *Hydrophilus* and *Dyticus*. In these beetles the muscles removed from the thorax, which have a reddish-yellow, or yellow colour, give a beautifully defined spectrum which is remarkable, in the first place, for the narrowness of its bands, and, in the second, from the fact that they differ totally from the bands of any decomposition product of hæmoglobin. Neither acid nor alkaline hæmatin, acid or alkaline hæmatoporphyrin, nor methæmoglobin, nor hæmochromogen, has the remotest resemblance to this pigment with regard to the spectrum. I next found this spectrum in the alar muscles of every insect which I examined, and afterwards in the voluntary and heart muscles of every vertebrate, it was then systematically traced throughout the whole animal kingdom.

To study the spectrum of myohæmatin uninfluenced by the presence of other pigments one has only to open the thorax of the meat-fly (*Musca vomitoria*), place the reddish yellow muscle in the compressorium, throw a good light through the object and examine with the miscrospectroscope. On doing this, three bands, two of which are of great narrowness, and beautifully sharp, are seen; the first is placed before the

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[*] *Cf.* GAMGEE's 'Physiological Chemistry,' and KÜHNE's 'Lehrbuch der physiologischen Chemie.'

[†] It is more correct to describe it as yellowish-red, and a concentrated solution, obtained by a method which I hope to describe shortly, is a *red* colour.

Fraunhofer line D, two others narrow and sharp, of which the second is darker than the first, between D and E, and generally two others nearer the violet (spectrum 10, Chart III.). The first three in the case of *Geotrupes stercorarius* read :—

1st band . . . λ 613 to λ 593,
2nd band . . . λ 567·5 „ λ 561·5,
3rd band . . . λ 554·5 „ λ 546,
4th band . . . λ 532 „ λ 511·5 (about).

In the alar and other voluntary muscles of other insects (and I have now examined a great number) myohæmatin is the pigment to which they owe their reddish-yellow or yellow colour. I do not think it necessary to give a drawing of the spectrum of myohæmatin in each case, as its bands always occur in the same part of the spectrum; besides anyone who possesses a microspectroscope can easily verify the truth of my statements for himself.

In *Hydrophilus piceus* and *Dyticus marginalis*, as already stated, the myohæmatin bands are seen with great distinctness, and in *Hydrophilus* early in 1883 I measured the bands in wave-lengths with the following result :—

1st band . . . λ 613 to λ 593
2nd band . . . λ 569 „ λ 563 } Approximate.
3rd band . . . λ 557 „ λ 548·5

The other bands could not be accurately determined. By heating this muscle in rectified spirit and caustic potash I obtained a small quantity of a yellow solution showing some feeble shading in green, and on adding sulphide of ammonium two bands like those of hæmochromogen came into view, but much nearer violet than those of hæmochromogen, thus the first extended from about λ 557 to λ 548·5, and evidently corresponded to the third band seen in the muscle. I would call attention to this fact, because a similar spectrum is seen in some insect muscles without any treatment, and it was also seen in a solution of isolated myohæmatin from vertebrates obtained by digesting the blood-free muscle in pepsine and water.* This kind of modified myohæmatin was met with in *Lucanus cervus*, as shown in spectrum 11, Chart III., also in some specimens of *Periplaneta orientalis*, in *Bombus terrestris*, and in *Apis mellifica*, in all of which species the unmodified myohæmatin also is found. In *Lucanus* these bands of changed myohæmatin read :—

1st band . . . λ 557 to λ 548·5,
2nd band . . . λ 532 „ λ 516 (?).

and therefore are placed in the same part of the spectrum as the third and fourth (?) bands of the normal myohæmatin spectrum.

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* See Chart IV., and *cf.* with spectrum of muscle of *Lucanus*, &c.

In *Cerambyx moschatus* the bands of myohæmatin became much more distinct after they had been treated with ammonium sulphide, and then read :—

1st band . . . λ 613 to λ 593,
2nd band . . . λ 570·5 „ λ 564·5, (?)
3rd band . . . λ 558·5 „ λ 551 (?).*

I noticed that the spectrum of these muscles became much feebler on exposure to air.

In *Creophilus maxillosus* the same four bands were well marked (spectrum 12, Chart III.).

In *Carabus violaceus*, of which a great number have been examined, the spectrum is equally satisfactory.

Although the muscle in *Coccinella bipunctata* is small in amount, yet the same spectrum was seen in it.

In *Periplaneta orientalis* we sometimes meet with the modified variety of myohæmatin of which the spectrum representing that of *Lucanus* is the same as in this, while in the bulk of the specimens examined the four-banded myohæmatin is present.

In *Staphylinus olens* whose testes, as already said, are coloured by hæmochromogen and possibly hæmoglobin, both the thoracic and leg muscles yield the spectrum of myohæmatin only.

Geotrupes stercorarius shows the myohæmatin spectrum in the thoracic and leg muscles beautifully marked. Spectrum 13, Chart III.

The wave-length measurements have been given above.

In *Gryllus domesticus* the thoracic muscle yields the same spectrum, and in the large thigh muscles it is well marked.

In dipterous, hymenopterous, and lepidopterous insects, those which use their muscles actively in moving the wings have the greatest amount of myohæmatin.

In *Tipula oleracea* although its thoracic muscle is small, it shows a beautifully defined myohæmatin spectrum; *Musca domestica*, *M. vomitoria*, and *M. chlora* are equally satisfactory; thus the alar muscle of a blue-bottle fly gave spectrum 10, Chart III.

In *Apis mellifica*, *Bombus terrestris*, and *Vespa vulgaris* myohæmatin is present abundantly. The alar muscle of *Bombus* sometimes shows the modified myohæmatin spectrum of which the bands in this case read :—

1st band . . . λ 556 to λ 550,
2nd band . . . λ 532 „ λ 513 (?).

In other specimens the normal spectrum was seen. (Spectra 14 and 15, Chart III.) The same remark applies to *Apis*.

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[*] Although (?) are placed after these it will be seen that they correspond closely enough with other measurements.

In those muscles of *Bombus* which contained the modified myohæmatin, treatment with ammonium sulphide developed the second myohæmatin band, but that before D could not be seen, *i.e.*, all the bands of the four-banded spectrum were present except the first. After the muscles of a moth had stood some time in glycerin the change into modified myohæmatin also took place, and on treating with ammonium sulphide the above-described change took place.

In *Acrida viridissima* I found myohæmatin present, but as in other orthopterous insects it is not present as abundantly as in dipters and lepidopters. On treatment with sulphide of ammonium the bands become much more distinct. (For *Periplaneta* and *Gryllus* see above.)

The diurnal and nocturnal lepidoptera show abundance of myohæmatin in their alar muscles, thus in *Pieris rapæ*, and other butterflies of which several have been examined, the spectrum is exactly the same as that described above. In various night moths, which need not be enumerated, it is present in abundance, and it also occurs in the mouth parts of various larvæ.

I have tried to isolate myohæmatin from insect muscle but without result, owing to dearth of material. After boiling in water, the solution appeared to have a faint bluish fluorescence, due probably to the presence of fine particles in suspension; and the muscle itself no longer showed the original spectrum but that of modified myohæmatin described above (except that the original spectrum was not restored with NH_4HS). The action of various solvents was tried in vain.

Acids cause the bands to disappear. Caustic alkalies (in strong solution) modify the spectrum when added to the solid muscle, the band before D disappears, another narrow band appears after D, and the dominant (3rd) band changes, being now made up of a lighter part nearer red, and a darker nearer violet; on treatment of the muscle (thus treated) with ammonium sulphide no noticeable change takes place. On treating the muscle of a moth with acetic acid the bands disappear, and on again adding caustic soda the bands appear as they do when caustic soda alone is used. With hydrochloric acid the bands also disappear, and on again adding caustic soda the third and fourth bands of the normal myohæmatin spectrum reappear, the spectrum thus reproduced resembling the modified spectrum described above.

When an attempt is made to mount an insect muscle in Canada balsam, the preliminary treatment destroys the bands, they are not much changed by being placed in alcohol, but in oil of cloves the bands completely disappear; this change is no doubt due to the ozonising action of the oil of cloves.*

On treating a muscle from a moth's thorax with peroxide of hydrogen the bands disappear, and the muscle is bleached by this treatment. On again treating with a reducing agent (*e.g.*, sulphide of ammonium) a new spectrum appears, the second and third myohæmatin bands having partially coalesced, and the second band being as dark as the third, the band before D being, however, well marked. Hence this change is not the same as that effected by acids. I have tried the effect of a current of oxygen passed over insect muscle placed in a suitable gas chamber placed beneath the microspectroscope; but, although the gas was passed for ten minutes, and the experiment several times repeated, the myohæmatin bands persisted. The reason, of course, may be that the gas did not penetrate the substance of the muscle, but merely passed over its surface.* Still the fact remains that exposure to air diminishes the intensity of the bands, that as I have found repeatedly the bands are less distinct when the insect is killed in flight, that when thus invisible, or nearly so, they can be brought back by the use of STOKES's fluid or ammonium sulphide. Hence, then, myohæmatin can be oxidised and reduced in the case of insects; its fully oxidised state is denoted by the absence of bands, its reduced state by their presence. The same was found to be the case with the histohæmatins, so that one may safely conclude that *these pigments are concerned in the respiration of the tissues in which they occur.*

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* In glycerin, specimens of muscle preserve the banded spectrum of myohæmatin for months, but it finally becomes altered into the modified variety. Insect muscle mounted in glycerin jelly soon changes as to the spectrum.

Myohæmatin also occurs in spiders. It is present in the muscle of the cephalothorax of *Epeira diadema*, *Tegenaria civilis*, and other spiders; in these the muscles are pale, and, therefore, contain but little myohæmatin, but its bands can generally be brought into view by treatment with reducing agents (spectrum 16, Chart III.).

In *Crustaceans* the distribution of myohæmatin is confined apparently to the cardiac muscle.

In all the specimens of *Astacus fluviatilis* examined the heart muscle showed the spectrum of myohæmatin, all five bands being visible. In the voluntary muscle it could not be found (spectrum 17, Chart III.).

In the heart of *Cancer pagurus* it is found, and it is absent from the other muscles (spectrum 18, Chart III.).

In the heart of *Homarus vulgaris* the myohæmatin bands could be measured in the large spectroscope and gave the following readings:—

1st band . . . λ 613 to λ 593,
2nd band . . . λ 569 „ λ 563 (about),
3rd band . . . λ 556 „ λ 550 (spectrum 1, Chart IV.).

It was absent in the voluntary muscle.

In *Pagurus bernhardus* it is present in the heart muscle, but as in the others absent from the voluntary muscle.

In *Carcinus mænas* the heart muscle† shows myohæmatin bands.

In all these cases the bands are made more distinct by the use of reducing agents and fainter by exposure to the air.

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* It is well known that the O in the O-hæmoglobin of vertebrate muscle is not given off *in vacuo*.

† But *not* the voluntary muscles.

Myohæmatin in Mollusca.

It occurs in all the pulmonates examined. Thus in *Limax flavus* the heart muscle shows it well; it is present more abundantly in the ventricle than in the auricle. It is present in the pharyngeal muscle of the same species (spectrum 2, 3, Chart IV.).

In *Arion ater* it is present both in the cardiac and pharyngeal muscle (spectrum 4, Chart IV.).

Limax maximus presents a beautiful myohæmatin spectrum in the ventricle of the heart, also in the pharyngeal muscle. In the heart and buccal muscles of *Helix aspersa* the myohæmatin bands are well marked (spectrum 5, Chart IV.). In the microspectroscope, as the drawings show, the bands are coincident with those of the myohæmatin of other species; owing to the smallness of the heart I could not measure these bands in wave-lengths, but there is no doubt that the measurements are the same. It also occurs in the heart and pharyngeal muscles of *Helix pomatia*.

*Myohæmatin in Vertebrates.**

The myohæmatin of vertebrates differs in no essential respect from that of invertebrates. In some cases the band before D is slightly narrower, or may sometimes (exceptionally) be double. The dominant bands are always the same.

Fishes.

In the mackerel (*Scomber scombrus*) myohæmatin occurs in the heart; it is well marked in the ventricle. In the pale dorsal muscles its presence is uncertain, in those along the lateral line, whose colour is brownish-red, it occurs mixed with some oxyhæmoglobin; in other parts of the lateral muscle it is well marked. (Chart IV., spectrum 6.)

In the herring (*Clupea heringus*) it is found in the ventricle (mixed with oxyhæmoglobin as in the mackerel). Its first band being somewhat narrower than usual; also in the auricle. It is mixed with oxyhæmoglobin in the more reddish parts of the dorsal muscles, and in the pale abdominal muscles it presence is uncertain.

In the roach (*Leuciscus rutilus*) it occurs in the ventricle of the heart mixed with oxyhæmoglobin, also in the muscle close to the lateral line; in the paler dorsal muscles its presence is uncertain, as is that of oxyhæmoglobin.

In the tench (*Tinca vulgaris*) it also occurs in the ventricle of heart mixed with oxyhæmoglobin. The dorsal (pale) muscle showed only traces of oxyhæmoglobin, the redder muscle along lateral line showed the same with traces of myohæmatin. In the tongue muscle only oxyhæmoglobin could be detected.

It has also been found in the heart muscle of the *plaice, eel, codfish, salmon, whiting, goldfish*, and others.

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* I have not thought it necessary to map the bands from the voluntary muscles as they are the same as in the heart of each animal examined.

Amphibians.

In *Bufo vulgaris* myohæmatin occurs in the heart, and in the voluntary muscles mixed with oxyhæmoglobin, it is well marked in those of the thigh. (Spectrum 8, Chart IV.)

In *Rana temporaria* it occurs well marked in the ventricle and feebly in the auricle, in both places mixed with oxyhæmoglobin. In faint traces in the thigh and calf muscles, which are very pale. Also in other muscles. (See spectrum 7, Chart IV.)

In *Salamandra maculosa* it is present mixed with oxyhæmoglobin in the ventricle; in traces in the arm and leg muscles and elsewhere in the voluntary muscles.

In the little green tree-frog (*Hyla arborea*) the distribution of myohæmatin was more carefully studied, and here I may observe that its absence must not be concluded from the fact that the muscle does not show the bands at once. If present in the oxidised state they may be invisible, so that a reducing agent may be necessary to bring them out. In most cases I used sulphide of ammonium in water or STOKES's fluid. It is present in *Hyla's* ventricle and in the auricle, in the flexors of thigh, and in its extensors; in the tongue muscles in traces; in the calf muscles; in the muscles in anterior aspect of leg; in the muscles of arm and forearm, and in all these apparently it is the sole pigment. It is mixed with oxyhæmoglobin in the muscles of the back and sometimes in those of tongue.

In the Axolotl (*Siredon pisciformis*) a feeble myohæmatin spectrum was seen in the ventricle and auricles, faint traces in the abdominal muscles, in those of the tail, and in the muscles of the leg; while in those of the tongue, and of the back only oxyhæmoglobin could be seen. In the "*red frog*" (species ?) myohæmatin occurs in the ventricle and in various voluntary muscles, *e.g.*, pectorals, muscles of thigh, of leg, and it was generally found mixed with oxyhæmoglobin.

Reptiles.

In a small mud turtle of the genus *Trionyx* the heart ventricle showed the myohæmatin bands so distinctly that I was able to measure them (approximately):—

1st band . . . λ 613 to 595,
2nd band . . . λ 569 „ 563,
3rd band . . . λ 556 „ 550. (See spectrum 9, Chart IV.)

The same bands are well marked in the pectoral muscles; and in those of leg and arm feebly.

In *Lacerta viridis* the same bands are well marked in the ventricle, and measured as follows:—

1st band . . . λ 613 to λ 593 (or λ 595),
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550,
4th band . . . λ 532 „ λ 513 (approximate).

In the flexor and extensor muscles of thigh, I could only find oxyhæmoglobin, in a muscle in front of pubis myohæmatin, in flexor muscles of forearm myohæmatin, in biceps and pectorals myohæmatin and oxyhæmoglobin, in calf muscles traces of myohæmatin, in those of tail only oxyhæmoglobin, in triceps and other extensors of arm myohæmatin and oxyhæmoglobin, in dorsal muscles only oxyhæmoglobin, and in depressors of mandible oxyhæmoglobin. In a second specimen the distribution was not quite the same, thus the tail muscles showed myohæmatin, the flexor muscles of arm myohæmatin and traces of oxyhæmoglobin, the same in its extensors; in flexors of thigh myohæmatin and oxyhæmoglobin, anterior muscle of leg the same, in calf muscles myohæmatin and oxyhæmoglobin, in mylohyoid both pigments, in thoracic intercostals only oxyhæmoglobin, in dorsal muscles both pigments, in tail muscles both pigments. This last lizard had its vessels injected with salt solution which partially accounts for the differences noted. (See spectrum 10, Chart IV.)

In *Emys Europæa* myohæmatin was found in auricle and ventricle, in the pectorals, in dorsal muscles traces mixed with oxyhæmoglobin, in tail muscles oxyhæmoglobin, the same in pelvic muscles, both pigments in the flexors and extensors of arm, and in the flexors and and extensors of leg.

In *Lacerta agilis* myohæmatin is well marked in the ventricular muscle, and in the biceps of arm; the redder parts of the flexors of forearm show the presence of oxyhæmoglobin, the paler myohæmatin; in the extensors only myohæmatin, the pectorals myohæmatin, in flexors of leg myohæmatin, the same in calf muscles, pelvic muscles traces of the same, muscles of tail oxyhæmoglobin and myohæmatin, dorsal muscles traces of myohæmatin, mylohyoid myohæmatin, and this pigment occurs well marked in the tongue muscles.

In *Scincus officinalis* myohæmatin is present in auricle and ventricle; and in the pectorals mixed with oxyhæmoglobin, in the triceps both pigments occur, in the tail muscles oxyhæmoglobin principally. In other muscles the distribution is much the same as in the above species. In *Tropidonotus natrix* the myohæmatin bands of auricles and ventricles give the following readings:—

1st band . . .	λ 613 to λ 593,
2nd band . . .	λ 569 ,, λ 563,
3rd band . . .	λ 556 ,, λ 550,
4th band . . .	λ 532 ,, λ 513. (?)

The same bands are well marked in the tongue muscles; in the mylohyoid and other muscles of mandible myohæmatin and oxyhæmoglobin are found, the latter, too, principally in the dorsal muscles and intercostals.

In a black snake (*Bascanium constrictor ?*) the same bands can be seen in the ventricle and auricle, in the muscles along the body both pigments occur, also in the depressors of the lower mandible, in the dorsal muscles, and in the intercostals. The bands of myohæmatin are badly marked in all these voluntary muscles.

Birds.

So far there is no difference in the spectrum of myohæmatin in all the animals examined. In birds and mammals the band at D may vary slightly, as will be seen when the spectra are described.

In the pigeon (*Columba livia*), while the dominant bands of myohæmatin are present in the ventricle of the heart that at D may be replaced by two; the same bands are seen in the auricle. In the pectorals and some leg muscles the band at D is the same as in the above-mentioned species; and in other voluntary muscles—where myohæmatin occurs generally with oxyhæmoglobin—this band is also similar.

In the snowy owl (*Nictea nivea*) the ventricle shows the usual myohæmatin spectrum (spectrum 11, Chart IV.), also the auricle. It is present abundantly in the pectoral muscles (as it is in all birds),* sparingly in the leg muscles, being apparently replaced to a great extent by oxyhæmoglobin.

In the *gizzards* of fowls I have found oxyhæmoglobin, whose second band is, however, slightly darker than it should be, probably from the presence of a trace of myohæmatin.

In the heart of the *common fowl* the band at D shows frequently the peculiarity noted above in the pigeon. Here the myohæmatin bands may be measured, and give the following result:—

1st band . . . λ 613 to λ 596·5, and shading λ 589 to λ 582,
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550 (approximate),

and these are well seen in auricle and ventricle.

In the ventricle of the *turkey's* heart the bands read:—

1st band . . . λ 613 to λ 593 (and shading ?),
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550.

In the auricle oxyhæmoglobin appears to be the dominant pigment.

In the auricle and ventricle of the *goose* the bands read:—

1st band . . . λ 613 to λ 593,
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550.

There are also two other bands nearer violet, too faint to be read. In the auricle and ventricle of the *duck* they give the same readings.

Putting M for myohæmatin and H for hæmoglobin, the following rough sketch will give an idea of the distribution of myohæmatin in the voluntary muscles of a bird (pigeon):—

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* In fact the pectorals of the pigeon are mainly, if not altogether, coloured by myohæmatin.

Biceps of forelimb, M and H; triceps, M and H; latissimus dorsi, M and traces of H; trapezius, M and H; muscles connecting skull to spine, M and H; tail muscles, H; flexors of forearm, M and H; extensors, M and H; sartorius (?), M and H; other thigh muscles, M and H; tibialis anticus, M and H; gastrocnemius, M; abdominal muscles, M and H; so that in all the voluntary muscles examined, we find myohæmatin, except in those of tail.

In the gizzard of the same bird there are also decided traces of myohæmatin, but oxyhæmoglobin is the pigment to which it mainly owes its red colour.

I have also examined other birds, and in all of them the results were the same as those described.

Mammals.

In the *hedgehog's* heart,—auricle, ventricle, and auricular appendix, all give the spectrum of myohæmatin. It also is found in most, if not all, the voluntary muscles mixed with oxyhæmoglobin. The same is the case in the *guinea-pig*, and in the *rabbit* (spectrum 12, Chart IV.); from an inspection of this spectrum it is seen that the bands are the same as those of myohæmatin found elsewhere, and give the same readings. The following will show the distribution of myohæmatin in the voluntary muscles of a rabbit; (putting H=Hæmoglobin and M=Myohæmatin):—Diaphragm principally H; pectoralis major, H and traces of M; sub-scapularis, H; intercostals, H; sterno mastoid, M and H; rectus abdominis, H; obliquus externus, H; latissimus dorsi, H; supra-spinatus, H and M; infra-spinatus, H and M; masseter, M and H; biceps of arm, M and H; triceps of arm, M and H; extensors of forearm, M and H; flexors of forearm, M and traces of H; psoas magnus, H; gluteus maximus, H and traces of M; rectus femoris, M and H; an adductor of thigh, H; vastus externus, M and H; gracilis, H; vastus internus, M and H; tibialis anticus, M and H; gastrocnemius (external head), M, and (internal), H; flexor communis digitorum, traces of M and H; other flexors of leg, ditto.

In the heart of the *hare* the band of myohæmatin at D of the normal spectrum is replaced by two (spectrum 13, Chart IV.), and these bands with the others gave approximately the following readings:—

1st band . . . λ 613 to λ 600, and shading λ 593 to λ 582. (?)
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550.

Here the inter-auricular septum gives both myohæmatin and oxyhæmoglobin, so does the auricular wall and appendix. In the ventricle, auricle, and auricular appendix of the *rat*, and in its voluntary muscles, the former pigment is found abundantly: in the ventricle the bands read (Chart IV., spectrum 15):—

1st band . . . λ 613 to λ 596·5,
2nd band . . . λ 569 „ λ 563,
3rd band . . . λ 556 „ λ 550.

In the *mouse* the bands are the same.

In the ventricle of the heart of the *dog*, the myohæmatin bands read (Chart IV., spectrum 14) :—

1st band . . . λ 613 to λ 598,
2nd band . . . λ 569 ,, λ 563,
3rd band . . . λ 556 ,, λ 550.

It is also present in the wall of auricle and auricular appendix, and in the general muscular system.

In the same parts of the *cat* it is found abundantly ; in the heart ventricle, after injection with salt solution, its bands read :—

1st band . . . λ 613 to λ 596·5,
2nd band . . . λ 569 ,, λ 563,
3rd band . . . λ 556 ,, λ 550.

In the *sheep*, *ox*, and *pig* it also occurs in the same situations, and, lastly, it has been found in the heart and voluntary muscles of man. Its bands are seen with great distinctness in the musculi papillares of the human heart, and here its first band is narrower than usual, as shown in spectrum 16, Chart IV.

Attempts to isolate Myohæmatin.

In myohæmatin the coloured constituent is united to a proteid as in hæmoglobin and enterohæmatin, hence the difficulty which attends its isolation. I have already described some experiments on the myohæmatin of insects ; on that of mammals a few experiments have also been made, but much yet remains to be done.

It was necessary to endeavour to find out what relationship it bears to muscle plasma, as KÜHNE[*] has shown that the hæmoglobin of muscle belongs to the plasma. Accordingly this experiment was performed : a rabbit was killed, the vessels at the base of the heart ligatured quickly, and both ventricles injected and well washed out with salt solution ; they were then quickly cut off at their junction with the auricles ; and after cutting them up, well washed with salt solution and put into a rag and frozen in a platinum vessel surrounded with a mixture of ice and salt ; when frozen they were removed and cut with an ice-cold knife, and pressure was then brought to bear on the mass in the rag ; a few drops of a reddish-yellow liquid exuded which was examined with the spectroscope. It showed the bands of oxyhæmoglobin which appeared to me slightly changed from the normal as the second one seemed too dark, and on adding sulphide of ammonium this idea was found to be correct, as now the dominant myohæmatin bands appeared in the usual position.

In some filtrate thus obtained, just above a freezing temperature spectrum 17, Chart IV., appeared after adding some sulphide of ammonium. Hence a part of this pigment occurs in the plasma like hæmoglobin. It is noticeable that its bands are merged into those of oxyhæmoglobin, which accounts for their having been missed by others; through the thin hazy band of reduced hæmoglobin they are, however, readily seen. I missed seeing the band at D, probably owing to the small amount of plasma at my disposal. I failed to get the pigmented part of myohæmatin by the use of any solvent into solution, thus the great pectoral muscle of a pigeon, which had been injected with salt solution, was cut up into small pieces, washed with salt solution and then strongly pressed; after a second washing and pressing it was divided and portions put into—(1) an aqueous solution of caustic soda; (2) a rectified spirit solution of caustic soda; (3) a rectified spirit solution with sulphuric acid; (4) amyl alcohol.

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[*] *Loc. cit.*

In the first solution I could find only hæmochromogen by the use of sulphide of ammonium: in the second a trace of changed myohæmatin by using the same reagent; in the third only acid hæmatin from the muscle hæmoglobin; and in the fourth a trace of lutein (= a lipochrome).

By boiling the same muscle in rectified spirit and sulphuric acid a spectrum was obtained which was a mixture of acid hæmatoporphyrin with a decomposition product of myohæmatin. The purple-red solution giving five bands, four of which read as follows:—

1st band . . . λ 640 to λ 623,
2nd band . . . λ 605 ,, λ 594, (or 3)
3rd band . . . λ 582 ,, λ 576, (?)
4th band . . . λ 563 ,, λ 545·5.

By similar *heating* with caustic soda and rectified spirit only hæmochromogen could be detected in the solution by adding ammonium sulphide.

(5) Ether failed to take up any pigment, also (6) benzol, but (7) chloroform took up a trace of a pigment, the solution being faintly yellow and showing a very narrow band in green and two belonging to lutein.

By the use of pepsine I succeeded in isolating a *changed* pigment. Some of the blood-free muscle from the ventricle of the heart of a sheep was cut up small, and after steeping in water for twelve hours, strongly pressed in a linen rag. This was now digested in a solution containing 0·6 per cent. oxalic acid (KÜHNE) and a little pepsine for two hours at a temperature of 98° F. This solution, after filtering, showed two bands having some resemblance to hæmochromogen, but placed nearer violet. They are evidently similar bands to those seen as an exception in the thoracic muscle of the bee and the cockroach, &c., *supra;* they read:—

1st band . . . λ 554·5 to λ 548·5,
2nd band . . . λ 524·5 ,, λ 519* (=narrow part).

On adding some caustic soda the bands disappeared, but with ammonium sulphide

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[*] This second band does *not*, however, correspond to that of altered myohæmatin.

they reappeared. Acetic acid did not seem to affect them. On examining the muscle thus treated I could still see a trace of the band before D, but the others had disappeared.

Some of the filtered pepsine extract was evaporated to dryness on the water-bath and left a *yellowish-red*, amorphous residue. This was insoluble in alcohol or chloroform (which each removed a trace of lutein, and other matters, but not the pigment), in benzol and light petroleum, but it easily went into *distilled water*, forming a yellow solution and giving the bands referred to above, and with sulphide of ammonium the bands were intensified (spectrum 18, Chart IV.), and read :—

1st band . . . λ 554·5 to λ 548·5,
2nd band . . . λ 524·5 „ λ 519.

There still remained in the dish traces of a purplish-brown pigment, which was probably changed myohæmatin, from the reaction obtained with it. By the use of trypsin digestion I failed to isolate the same pigment.

I succeeded in isolating the same pigment from the pectoral muscle of a pigeon, and got the above results. Hence any attempt at isolation alters the nature of the pigment, except freezing. But we may so far conclude that myhoæmatin is a yellow or reddish-yellow pigment, and when isolated and changed soluble only in water.

I hope to continue these experiments shortly.

The Hæmochromogen of the Medulla of the Adrenals and the Pathology of ADDISON'S *Disease.*

In the adrenals, as already shown, we meet with a spectrum which is totally different from that of the histohæmatins, for while in their cortex a histohæmatin may be present, in the medulla *free* hæmochromogen occurs. A similar spectrum may be met with occasionally in the liver, and perhaps in the spleen. Its bands are certainly diminished after the injection of salt solution, hence here the hæmochromogen must be looked upon as an excretion. This spectrum is very constant, and so far I have found it in the adrenals of man, dog, cat, rabbit, rat, guinea-pig, ox, and sheep. VULPIAN has shown that taurocholic acid exists in the medulla,* and other observers have found products which indicate the existence of an active downward metabolism. Taken in connexion with my own observations these facts go to prove that the adrenals are organs which are concerned in the retrogressive metamorphosis of hæmoglobin, and probably of the pigments described in this paper—the histohæmatins and myohæmatin. Hence if the adrenals are not in a fit state for the discharge of their functions we may have pigments present in the circulation which are incompletely metabolised. Now, I have shown that such is the case, as the urine of ADDISON'S disease may contain a pigment which I formerly described under the name of "urohæmatin,"[*] which is a pigment closely related to hæmatoporphyrin, and which may also appear in the urine when the adrenals are healthy if there be an excessive destruction of blood-corpuscles, as in acute rheumatism; in such cases there being more effete colouring matters present than the organs concerned in their further downward metamorphosis are capable of dealing with. I need not describe the characters of urohæmatin more fully here, as I have done so elsewhere,[†] but merely call attention to the significance of its presence.

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* Other constituents are leucin, hypoxanthin, benzoic and hippuric acids, taurin, &c.

Recent researches[‡] on the development of the adrenals go to negative the idea that they are nervous ganglia, and I believe they may be looked upon as organs which are more or less supplementary to the liver, which have been developed at a later stage (*i.e.*, a later stage in the ancestral development), when the animal body had become more complex, and a greater abundance of respiratory pigments had become necessary for internal and ordinary respiration; which entailed the setting apart of certain organs to carry on the increased "division of labour;" in this case the function of these supplementary organs being the removal from the circulation of useless and worn-out pigments, and their accompanying proteids.

Whether this view be correct or not, it fits in well with the teachings of physiology and pathology. For TIZZONI has shown that the removal of the adrenals is followed by pigmentation of the skin and mucous membranes, and in the majority of cases of ADDISON's disease in which well-marked bronzing of the skin took place they have been found diseased. The occurrence of ADDISON's disease without apparent disease of the adrenals can be easily explained on the hypothesis that they are supplementary organs, as other organs may do duty for them, but it remains to be proved whether, when they are apparently healthy in cases of bronzing of the skin, other conditions may not be present which hinder the discharge of their functions, such as obliteration of their arterial or nervous supply.

No sufficient explanation has yet been offered as to the causation of ADDISON's disease, and if the facts described in this paper should help to solve this problem it may induce others to follow up these observations, which at first sight seemed to have but the remotest bearing on human pathology. I have tried to obtain pigments from the adrenals by the use of various solvents, but as yet without result.

Are there any grounds for supposing that the product of their metabolic activity may be derived from the histohæmatins? I believe this question may be answered in the affirmative for this reason, that in the integument of *Uraster rubens*, as already mentioned, hæmatoporphyrin occurs *as such*, and here it is highly probable that it is a derivative of the histohæmatins, for in *Uraster* besides the lipochromes and enterochlorophyll, these are its only available source. This hæmatoporphyrin is nearly related to the urohæmatin found in ADDISON's disease, as I have already stated. Hæmatoporphyrin also occurs (as I have shown) in the integument of *Limax* and *Arion*,* and in their bodies again it is probably derived from the histohæmatins and possibly from enterohæmatin. Enterohæmatin presents same remarkable resemblance to myohæmatin. (1) Neither can be converted into all the decomposition products of hæmoglobin. (2) Both are composed of a proteid and colouring matter united together. (3) In both acids cause the bands to disappear. (4) In both potassium hydroxide and sodium hydroxide intensify the bands. (5) In both the banded condition belongs to the reduced state and the bandless to the oxidised. Again myohæmatin can be changed into a body which closely resembles (in its spectrum) enterohæmatin. Hence in saying that enterohæmatin may be the mother-substance of the integumental hæmatoporphyrin, is practically the same as saying that it may be derived from the histohæmatins.

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[*] Proc. Roy. Soc., vol. 31, p. 26, and vol. 35, p. 394; also 'Journal of Physiology,' vol. vi., pp. 22 *et seq.*

[†] *Loc. cit.*

[‡] Compare W. F. R. WELDON "On the Supra-renal Bodies of Vertebrates," Quart. Journ. Micros. Soc., vol. xxv., pp. 137 *et seq.*; also BALFOUR's "Treatise on Comparative Embryology;" and ALLEN THOMSON in the 9th Edition of "QUAIN's Anatomy."

I have endeavoured to find out if anything like myohæmatin could be prepared from any of the decomposition products of hæmoglobin, but without any definite result. In a solution of alkaline hæmatoporphyrin (in rectified spirit and ammonia) a change took place spontaneously, after the solution had been shut up from air and light for some months; the four-banded spectrum disappeared and could not be regenerated, and in its place I observed some narrow bands closely resembling those of myohæmatin, but placed much nearer the red end of the spectrum. They were narrower than those of any other decomposition product of hæmoglobin, but the solubility of the pigment and its refusal to be reduced, showed that it was not myohæmatin. Acting on this hint, I tried the effect of various oxidising and reducing agents on hæmatin and hæmatoporphyrin, but no myohæmatin-like spectrum could be obtained; but it is probable that myohæmatin is much nearer to hæmoglobin than to hæmatoporphyrin, and the above may be an accidental resemblance.

The Function of the Histohæmatins and Myohæmatin.

I need not repeat the results obtained by the action of oxidising and reducing agents on these pigments, it will suffice to say that they are capable of oxidation and reduction, and are hence respiratory. Just as in *Actiniæ*—as I have shown in a former paper,—actiniohæmatin is concerned in the respiration of the tissues, so these pigments are also concerned in it. They combine with the oxygen conveyed to them in the blood, and hold it for purposes of metabolism, parting with the carbon dioxide in exchange for the oxygen. This is the only conclusion which anyone who has gone over the same ground can come to. These observations appear to me to point to the fact that the formation of CO_2 and the absorption of oxygen takes place *in the tissues* themselves (PFLÜGER and OERTMANN) and not in the blood. Hence these observations are of value in helping to decide a difficult point. I have not succeeded yet in finding out whether these pigments are dissolved in the plasma bathing the tissues, or in the *solid* parts of the tissues. In the case of muscle, certainly a small amount of myohæmatin was obtained from the plasma, but after squeezing out all juice, the muscular fibre showed abundance of myohæmatin, which at the same time may have been prevented exuding by coagulation of the myosin. I am inclined to believe that a certain amount of myohæmatin belongs to the *solid* (or semi-solid) part of the muscular fibre, and probably the same remark applies to muscle hæmoglobin; for after all the opposite conclusion is mainly based on KÜHNE and EBERTH's observation of the presence of a living nematode within the sarcolemma, and this does not altogether exclude the possibility of the presence of a colouring matter in the sarcous substance.

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* Proc. Birm. Phil. Soc., vol. iii., pp. 351–407; Journ. Physiol., vol. vi., pp. 22–39, and vol. vii., pp. 240 *et seq.*

I have not insisted strongly on the fact that myohæmatin is a histohæmatin, as anyone cannot fail to come to that conclusion who studies the accompanying charts. Myohæmatin then may be considered as the true intrinsic colouring matter of muscle, and the histohæmatins the intrinsic colouring matters of the tissues and organs; both may be reinforced or replaced at times by hæmoglobin when extra activity of internal respiration is required; probably the same radical may be made use of for building up all these pigments, at all events they seem to be related, since the same decomposition product—hæmatoporphyrin—is probably yielded by all of them. The fact that in the lower animals pigments of less complex molecular structure than hæmoglobin and identical with its decomposition products can function like it, forces itself on anyone's attention who studies the pigments of the Invertebrata.

Lastly, I would call attention to another striking fact which I have found out, thanks to Professor MOSELEY. In his most valuable Paper* on "animal colouring matters," which he discovered while on board the "Challenger," he describes a madder-coloured pigment named by him polyperythrin, and he suggested that it might have some connexion with some of the pigments found by me in *Actiniæ*.† It was found by Professor MOSELEY in simple stony corals of very different genera, in two forms of Actiniæ from deep water, and in certain hydroids. In the drawing accompanying Professor MOSELEY's Paper he figures an acid and an alkaline spectrum, and it will be noticed how these spectra resemble acid and alkaline hæmatoporphyrin respectively. On examining some slides of the dried pigment kindly sent by Professor MOSELEY, I found that the bands of the neutral dried pigment corresponded very closely (although not exactly) to those seen in artificially-prepared neutral hæmatoporphyrin, and in that obtained from the integument of *Uraster rubens*, &c., and still more closely to the bands in the egg-shell of a Cochin China hen.‡ Moreover, with good illumination, a fourth band can be seen nearer the violet which is also present in the spectrum of neutral hæmatoporphyrin. Hence polyperythrin is closely related to, if not identical with, hæmatoprophyrin, and is closely related to my actiniohæmatin, as this can also be made to yield hæmatoporphyrin; so that all these observations fit into each other, and show, what I have endeavoured to point out, that in the lower animals we meet with pigments which resemble, or are identical with, decomposition products of hæmoglobin, and yet are built up from a body of less complex constitution than it is.*

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* "On the Colouring Matters of Various Animals," &c., Quart. Journ. Micros. Soc., vol. xvii., N.S., pp. 1-23.

† "Chromatology of Actiniæ," Phil. Trans., vol. 176, p. 641.

‡ In which, as in many other birds' shells, hæmatoporphyrin occurs as such. For a list of the animals in which polyperythrin was found, see Professor MOSELEY's Paper, *loc. cit.* [Since the above was

In conclusion, I beg to thank the Government Grant Committee of the Royal Society for the grant which enabled me to purchase the instruments, reagents, and specimens required for this research.

EXPLANATION OF THE CHARTS.

CHART I., PLATE 11.

Sp. 1. Histohæmatin in the ovary of *Uraster rubens*.
Sp. 2. Modified histohæmatin in its stomach-wall.
Sp. 3. Histohæmatin in foot of *Littorina littorea*.
Sp. 4. Do. in foot of *Purpura lapillus*.
Sp. 5. Do. in mantle of *Mytilus edulis*,
Sp. 6. Do. in ovary of same.
Sp. 7. Spectrum of *receptaculum seminis* of *Helix aspersa*.
Sp. 8. Histohæmatin in the nephridium of *Limax flavus*.
Sp. 9. Do. in the nephridium of another *Helix*.
Sp. 10. Do. in the albumen gland of *Limax*.
Sp. 11. Do. in the *vas deferens* of same.
Sp. 12. Do. in stomach-wall of *Astacus fluviatilis*.
Sp. 13. Modified histohæmatin in the stomach-wall of another *Astacus*.
Sp. 14. Histohæmatin in green gland of *Astacus*.
Sp. 15. Do, in the branchiæ of some specimens of same,
Sp. 16. Do. in the green gland of *Homarus vulgaris*.
Sp. 17. Hæmochromogen-like spectrum in the testes of the beetle, *Staphylinus olens*.

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written I have found hæmatoporphyrin in *Lumbricus*, and proved its identity with polyperythrin. See 'Journal of Physiology,' vol. vii., pp. 240 *et seq.*—June 16, 1886.]

* Perhaps the great molecular complexity of hæmoglobin is due more to its proteid than its coloured constituent. H. STRUVE tries to show that one of the *colouring matters* of hæmoglobin is a feeble acid probably combined in the blood with soda or some organic base, and proposes to name it *hæmatic acid*, another agrees with HOPPE-SEYLER'S hæmatin. (= hæmic acid of STRUVE). The blood-crystals would be, therefore, crystals of a blood-albumin coloured by these acids. Journ. prakt. Chemie, [2], xxix., 305.

CHART II., PLATE 11.

Sp. 1. Histohæmatin in kidney and liver of *Tinca vulgaris.*
Sp. 2. Do. in stomach wall of *Rana temporaria.*
Sp. 3. Do. in liver of Axolotl (*Siredon pisciformis*).
Sp. 4. Do. in kidney of same.
Sp. 5. Histohæmatin in stomach-wall of same.
Sp. 6. Do. in kidney of *Trionyx.*
Sp. 7. Do. in stomach-wall of *Emys Europæa.*
Sp. 8. Do. in kidney of *Lacerta viridis.*
Sp. 9. Do. in stomach-wall of same.
Sp. 10. Do. in liver of same.
Sp. 11. Do. in kidney of pigeon (*Columba livia*).
Sp. 12. Do. in kidney of the snowy owl (*Nictea nivea*).
Sp. 13. Do. in kidney of the *Guinea-pig.*
Sp. 14. The hæmochromogen-like spectrum of the medulla of the adrenals of same animal.
Sp. 15. Histohæmatin in the intermediate zone of same adrenal.
Sp. 16. Do. in the blood-free cortex of kidney of *Rat.*
Sp. 17. Do. in the stomach-wall of same.

CHART III., PLATE 12.

Sp. 1. Histohæmatin in liver of *Rabbit.*
Sp. 2. The hæmochromogen spectrum in the medulla of adrenal of same animal.
Sp. 3. Histohæmatin in the kidney of same.
Sp. 4. Do. in blood-free stomach wall of *Cat.*
Sp. 5. Do. in blood-free pancreas of same.
Sp. 6. Do. in blood-free liver of same.
Sp. 7. Do. in blood-free kidney of same.
Sp. 8. Spectrum of same animal's ovary blood-free.
Sp. 9. Enfeeblement of hæmochromogen bands in medulla of adrenals of same animal after injection with salt solution.
Sp. 10. Myohæmatin of *Musca vomitoria.*
Sp. 11. Modified myohæmatin from *Lucanus cervus.*
Sp. 12. Myohæmatin of *Creophilus maxillosus.*
Sp. 13. Do. of *Geotrupes stercorarius.*
Sp. 14. Modified myohæmatin in *Bombus terrestris.*
Sp. 15. Normal myohæmatin in same species.

Sp. 16. Myohæmatin in the spider—*Tegenaria civilis*.
Sp. 17. Do. in the heart of *Astacus fluviatilis*.
Sp. 18. Do. in the heart of *Cancer pagurus*.

CHART IV., PLATE 12.

Sp. 1. Myohæmatin in the heart of *Homarus vulgaris*.
Sp. 2. Do. in the heart of *Limax flavus*.
Sp. 3. Do. in the pharyngeal muscles of same.
Sp. 4. Do. in both situations in *Arion ater*.
Sp. 5. Do. in the heart of *Helix aspersa*.
Sp. 6. Do. in the heart ventricle of a mackerel (*Scomber*).
Sp. 7. Do. in the heart of *Rana temporaria*.
Sp. 8. Do. in the heart of *Bufo vulgaris*.
Sp. 9. Do. in the heart of a *Trionyx*.
Sp. 10. Do. in the heart of *Lacerta viridis*.
Sp. 11. Do. in the heart of snowy owl (*Nictea nivea*).
Sp. 12. Do. in the heart of a *Guinea-pig*.
Sp. 13. Do. in the heart of a *Hare*.
Sp. 14. Do. in the heart of a *Dog*.
Sp. 15. Do. in the heart of a *Rat*.
Sp. 16. Do. in a *musculus papillaris* of *human* heart.
Sp. 17. Isolated myohæmatin in muscle plasma.
Sp. 18. Changed myohæmatin isolated by pepsine, in water, treated with NH_4HS.

VII. *An Experimental Investigation into the Form of the Wave Surface of Quartz.*

By JAMES C. MCCONNEL, *B.A.*

Communicated by R. T. GLAZEBROOK, *M.A., F.R.S.*

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I.—INTRODUCTORY REMARKS.

ABOUT two years ago I read a paper before the Cambridge Philosophical Society describing some measurements of the "dark rings" in quartz. The present paper contains an account of similar measurements made with greatly improved apparatus, and extending over a much larger field. These "dark rings" supply a delicate method of determining the retardation of the extraordinary wave behind the ordinary in the crystal and consequently the separation between the two sheets at various points of the wave-surface.

In quartz the wave-surface may be nearly represented by a prolate spheroid surrounded by a sphere passing through the extremities of its axis. The spheroid is slightly flattened at the extremity of its axis and the sphere slightly bulged, so that the two no longer touch. The distance between the two at the extremity of the axis we know very accurately from observations on the rotatory power, while the two radii at the equator of the wave-surface are known from observations with the spectrometer.

In all the theories on the subject these three constants are assumed; so the theoretical surfaces are made to coincide with the true one in the equatorial section and to give the true distance between the two sheets at the extremity of the axis. At intermediate points their correspondence with the true surface lies open to the test of experiment. My former observations were confined to the regions near the axis, as it is only there that the bulging and flattening are at all conspicuous. But the increased facilities ot a new arrangement for measuring the rings led me to extend my observations over the whole surface, so that I have now determined the gradually increasing distance between the two sheets from the axis to the equator.

This was the more necessary because the known values of the radii of the equatorial section, or, in other words, of the principal wave-velocities, are not sufficiently accurate to give a good measure of their difference. And it is upon this difference that the theoretical distance between the two sheets, even in the region near the axis, to a great extent depends.

It will be well to give at this point some idea of the relative magnitudes involved. The difference between the equatorial radii is about $\frac{1}{200}$th part and the distance between the sheets at the extremity of the axis $\frac{1}{20000}$th part of the radius of the sphere. My determination of the distance between the sheets should not at any rate be in error by more than one part in 500 at 4° from the axis, one part in 1000 at 12°, and one part in 2000 at a considerable distance from the axis. Of that, though by no means a complete investigation of the form of the wave-surface, these observations must be admitted to be a severe test. For if one wave-velocity were to be changed while the other remained the same, the change would be indicated even though it should only amount to $\frac{1}{400000}$th part of the whole velocity. Indeed near the axis $\frac{1}{8000000}$th part would be sensible.

The theory of the formation of the rings requires some consideration. Take a wave-front of the plane polarised incident light. By the refraction at the first surface it is resolved into two wave-fronts which are polarised in a manner dependent on the constitution of the crystal, and which travel with different velocities. Each of these on refraction at the second surface gives rise to a wave-front polarised in a manner somewhat different from its own. Let the emergent wave-front due to the extraordinary wave be B and the other A. Then B and A are parallel. If B be in advance of A by an integral number of wave-lengths, A will be coincident with a wave-front exactly similar to B, and in the same phase. But we cannot say that, therefore, the combination of these two will be exactly similar to or even polarised in the same manner as the incident wave-front, for there has been loss of light by reflection at both surfaces, and this has affected A and B differently.

The consideration of the refractive effects is greatly simplified in our case by the circumstance that the optic axis lies in the plane of incidence. Thus the principal axes of the ellipses of vibration of the waves in the quartz lie respectively in, and perpendicular to, the plane of incidence.

We will assume at present that the action at the surface produces no retardation of phase. Let us first suppose that the incident light is plane polarised and the vibration lies in the plane of incidence. This linear vibration on entering the crystal gives rise to two elliptic vibrations; and we may, I think, safely assume that, if the relative retardation amount to an integral number of wave-lengths these two elliptic vibrations will give rise on emergence to a single linear vibration also in the plane of incidence. For we may consider the components of these two elliptic vibrations perpendicular to the plane of incidence as due to two equal and opposite linear vibrations of the incident light. These two linear vibrations would suffer equal reductions at the first refraction, and equal reductions at the second refraction, so after both refractions they would again neutralise each other. It is indeed probable that the difference in the angle of refraction of the two waves would affect the amount of light lost by reflection, but it would be to a negligibly small extent. Thus the emergent light will be sensibly plane polarised.

Similarly, if the vibration of the incident light be perpendicular to the plane of incidence, the emergent light will be also plane polarised. Consequently, if the incident light be plane polarised in any plane, the emergent light will also be plane polarised, though not necessarily in a parallel plane. Thus, for angles of incidence giving a relative retardation of an integral number of wave-lengths, the refractive effects are equivalent to a small rotation of the plane of polarisation of the incident light. And the same is no doubt very approximately true for neighbouring angles of incidence. This small rotation can, as will appear later on, be eliminated by taking the mean of two sets of observations.

Up to this point, and indeed throughout, we assume that there is no perceptible retardation of phase at the surface. Careful observations have been made on glass with regard to this point, and the only trace of retardation found was at very high angles of incidence, and even that was highly doubtful. There seems to be no reason to expect such an effect in crystalline media more than in isotropic, at any rate when the rotatory effects are small. In the present case too the rings are very close together at the high angles of incidence, so that only a small error would result; *e.g.*, at an incidence of 75°, which is the highest incidence I have reached, the error in the diameter of a ring produced by a retardation of $\frac{\lambda}{100}$ would be only $\frac{1}{2}'$. As to any surface retardation connected with the rotatory power, we know from measurements of the rotation in plates of different thickness that it is, at any rate, very small when the light is incident normally, and passes along the axis. These measurements have been made with great accuracy, and no such effect has been even suspected. So we have a maximum limit for it, from which I deduce that it could only make itself felt slightly in the first ring, in the others not at all.

II.—THE APPARATUS AND MEASUREMENTS.

My previous observations were made with one of GROTH'S polariscopes somewhat modified, as described in the paper, but since then I have found it a great improvement to use instead an ordinary spectrometer. With some slight additions the spectrometer became a most efficient instrument for measuring the rings.

[redacted]

The general arrangement is indicated in fig. 1. The source of light is a BUNSEN flame in the edge of which is placed a bead of sodium carbonate. The light is polarised by the NICOL A and screens are placed so that no other light can reach the eye. The slit of the collimator has been removed so the light falls on the whole breadth of the object glass B of the collimator. Here it is transformed into a convergent beam which passes through the quartz plate C. Each parallel pencil emerging from the quartz is brought to a focus in the focal plane of the object-glass D. So the needle-point E has to be carefully adjusted to lie in this plane. In this particular the spectrometer has a great advantage over the polariscope. The focal length is much greater and so the adjustment can be made with greater accuracy, and the spherical aberration, which in the polariscope is very troublesome, is so small as to produce no sensible error. F is the eye-piece and G the second NICOL by which the light is analysed.

I found that the ordinary eye-piece magnified too strongly, so I substituted a single lens and fitted it up with the NICOL G in a large cork, so that the combination could be readily exchanged for the ordinary eye-piece without disturbing the needle-point. Even with the low power the apparent size of the rings was vastly greater than with the polariscope. This was mainly due to the greater focal length D E, which was about nine inches. Though the definition of the rings suffered with the increased magnification, there was on the whole a decided gain in accuracy, and the observations became far less trying to the eyes. The spectrometer table too was furnished with a slow motion screw which was no small advantage. The spectrometer was fitted with a circle graduated on silver, and both the telescope and table were provided with verniers reading to half minutes. By replacing the slit and the ordinary eye-piece of the telescope the spectrometer could return to its ordinary use. The normal to the faces of the quartz could thus be set at right angles to the axis of rotation of telescope and table and its position determined relatively to the axis of collimation of the telescope for any given readings of the telescope and table verniers. For levelling purposes the quartz was mounted on a tripod stand resting on three adjustable screws whose rounded ends rested in a conical hole, in a V-shaped slot, and on a smooth surface, respectively on the table of the spectrometer. Each screw carried a loose nut which, when the screw had been properly adjusted, could be screwed down tight onto the tripod. This made the three screws a perfectly firm support and the tripod could be removed from the table and replaced accurately in its original position—a great convenience.

The distance A B from the polarising NICOL to the object-glass of the collimator was over four feet, so the light which fell on the lens B had passed through the NICOL nearly as a parallel pencil, and therefore was polarised approximately all in one plane. The two NICOLS could therefore be crossed with greater accuracy. In order to cross the NICOLS the quartz was removed and the cork turned till the light was quenched. In my earlier observations I simply used the sodium light for this purpose, but I found that this led to errors of two or three minutes in the smaller rings, so the crossing for all the observations given below was performed with a gas-flame placed edgeways behind the polariser. This gave ample accuracy.

[*Added May* 31, 1886.—Probably the lenses had some slight doubly refracting power, so that each turned the plane of polarisation through a small angle depending on its azimuth. In the present case however this effect was a matter of indifference, as I was measuring the angles of incidence, for which the emergent light from the quartz was polarised similarly to the incident light. In the larger rings, it is true, the quartz produced a considerable lateral displacement of the light, so it no longer passed centrically through the two object glasses. But in the larger rings the effect of any small error of crossing might, as will be seen shortly, be completely neglected.]

The plane of polarisation was inclined at 45° to the plane of incidence. If we look at the appearance presented in the polariscope when the two NICOLS are crossed, we see that all the rings are circular, and though the inner rings are tolerably uniform, the outer rings are crossed by dark brushes in directions parallel and perpendicular to the plane of polarisation. These dark brushes have the effect of making the rings very ill-defined, so that on that account alone it would be impossible to get a satisfactory measure of the 15th ring if the plane of polarisation were parallel to the plane of incidence. If now we rotate the analyser slightly we see the rings dilate, but not uniformly. The dilatation is much more rapid in the direction of the brushes. The rings cease to be circular and become four-cornered. This phenomenon was observed and explained by Sir GEORGE AIRY (Camb. Phil. Trans., vol. 4, p. 85).

It is an easy deduction from his formula for the intensity at any point of the field that the value of R for the darkest part of the ring when the NICOLS are not accurately crossed is given by

$$\sin\frac{2\,\mathrm{R}\pi}{\lambda}=\frac{2\sin\delta}{\sin 2\gamma}$$

in the direction of the brushes, but by

$$\sin\frac{2\,\mathrm{R}\pi}{\lambda}=2\sin\delta\sin 2\gamma$$

in directions at 45° to the brushes. Where R is the relative retardation, δ is the small angular error of crossing, and $\tan\gamma$ is the ratio of the axes of the ellipse of vibration of either wave, $\tan\gamma$ being less than unity. The following figures will give some idea of the values of γ. For sodium light when—

$$\begin{array}{ll}\phi=1^\circ & \gamma=43^\circ\,53' \\ \phi=5^\circ & \gamma=23^\circ\,0' \\ \phi=10^\circ & \gamma=7^\circ\,21' \\ \phi=20^\circ & \gamma=1^\circ\,55'\end{array}$$

ϕ being the angle between the wave normal and the optic axis.

[When $\delta=0$, $R=n\lambda$, n being an integer; as is obvious *à priori*. Now the change in the relative retardation necessary to produce a ring gives a fair indication of the change in the radius of the ring.*] So for the larger rings, while the displacement of the ring in the 45° directions, due to a small error in crossing, is almost nil, the displacement in the parallel and perpendicular directions is extremely large. The latter, however, is masked by the general obscurity of the brushes. From this it is clear that the best position for the plane of polarisation is at an inclination of 45° to the plane of incidence.

It occurred to me, as an objection that might be of importance, that there would be some rotation of the plane of polarisation through refraction at the surface of the quartz and the surfaces of the lenses, and that putting the plane of polarisation in the 45° position made this rotation as large as possible. But it is easy to see that if the polariser and analyser be turned into the other 45° position the rotation will be in the opposite direction. Thus in one case the rings will be slightly too large, in the other just as much too small, and by taking the mean of the two the error will be eliminated. I have, therefore, taken observations throughout in these two positions of the polariser, though no effect of the kind has made itself manifest.

The first set of observations recorded below were made on a piece of quartz, which I will call Plate 1. It has four polished faces, and the section perpendicular to these faces has the figure of an equilateral triangle described on a square. The two sides of the square adjacent to the triangle were polished faces forming a parallel-sided plate. The two other faces were convenient as supplying a definite plane of reference passing through the normal to the two plate faces, though they were originally cut for quite a different purpose. Each face was about an inch square. The whole piece was perfectly clear, and the only flaw was a slight intrusion of contrary quartz into one corner. The plate faces were very nearly parallel planes, the error of planitude not exceeding 1′, and the error of parallelism not exceeding 2′. Measurements of the rings were made in two different planes. The plane which is perpendicular to all four faces I will call plane A. The plane at right angles to plane A I will call plane B. The four polished faces were very nearly in the same zone.

The observations in plane A were made in the following order. The quartz was fixed on the tripod and all four faces set parallel to the axis of rotation of the spectrometer in the usual way by means of reflections from the faces. Readings were also taken from which I could find the position of the normal to one of the plate faces relative to the axis of the telescope for any given readings of the telescope and table verniers. The tripod and quartz were then lifted off the table, the slit removed from the collimator, the ordinary eye-piece of the telescope replaced by the cork containing the low power eye-piece and analyser, the gas-flame placed behind the polariser, and the NICOLS crossed. The tripod having been returned to its old position and the gas-flame exchanged for the sodium-flame every-thing was ready for observation. The temperature was taken, usually at the beginning and end of a set of observations, from a thermometer lying on the table by the side of the spectrometer.

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* Added May 31, 1886.

The appearance seen in the telescope was the needle-point standing out against an irregular patch of light crossed by one or more dark bands. The bright patch was really the aperture of the analysing NICOL, and as the telescope was moved round one or two degrees the patch moved across the needle-point. This was due to the light which reached the eye coming from a different part of the object-glass and thus passing in a different direction through the analyser.* Thus it was really equivalent to a slight rotation of the analyser round its axis. A similar effect was produced by turning the table owing to the lateral displacement of the beam of light by the quartz. To avoid the latter evil I at first always turned the telescope till the needle-point was exactly in the centre of the patch before I took a reading. This was done in most of the observations on Plate 1. But for the small rings in Plate 2 I simply clamped the telescope in the position where the NICOLS were crossed, and kept it there. By trying exaggerated cases I found the error was very small and it tended to increase the radius on one side while diminishing it on the other.

The rings of course were fixed relatively to the quartz, so that the difference of the readings of the table vernier for the two sides of the ring being on the needle-point gave the diameter of the ring in air.

For the first half dozen rings it may be shown, that the mean of these two readings should coincide, or in other words that the rings are practically circular and have a common centre, provided that the deviation of the axis from the normal do not exceed two or three degrees. This common centre may be called the axis in air, and is related to the real optic axis by the ordinary law of refraction. From this it is easy to see how the deviation of the axis from the normal was determined from the measurements of the rings. I found that the error was 1° 45′ measured parallel to plane A and 18′ measured perpendicular to plane A. It is clear since the axis lay 18′ out of plane A that instead of measuring the diameter of a ring I was only measuring a chord. The small correction for this was however easy to apply.

But for the measurements at right angles to plane A this chord would have been perhaps only half the diameter for the first ring if I had proceeded as before. It was necessary to tilt the plate forwards till the axis in air came nearly into the plane of measurement. I was at a loss for some time how to produce this large tilt on the spectrometer with any accuracy. At last I hit upon the following expedient. I fixed a small piece of silvered glass on to one side of the plate so as to be approximately in the same zone as the four faces and approximately perpendicular to the axis in air. I first fixed it in its place with soft wax, adjusting it with my eye at the telescope, and then secured it firmly by pouring in electrical cement behind it. After this was attached, it was only necessary to bring its normal into the plane of measurement to secure that the diametral chord was being measured. Plane B then may be defined as passing through this normal and being approximately perpendicular to plane A.

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* When the direction of light incident on a NICOL'S prism is inclined to the principal plane of the prism at an angle α, then, in order that the light may be completely quenched by the prism, its plane of polarisation must be inclined at an angle $\alpha/3$ nearly, to the plane through the ray most nearly parallel to the principal plane of the prism. See a paper by the author, Phil. Mag., vol. 19 (1885), p. 320.—[June 15, 1886.]

The first ring was considerably broader and less sharply defined than the others; yet in obtaining the diameters recorded in the tables below I have relied on a single reading of each side even of the first ring. For during a long course of preliminary measurements I had found, that two readings of the first ring would seldom differ more than ½′, though I could not be confident that the true reading lay within ½′ of either. It seemed in fact to be easier to bring the needle back to the same point in the band than to make sure of that point being the middle of the band. To obtain real accuracy I relied on varying the conditions as much as possible. Thus the four sets of measurements recorded in Table I. were made on four different days with different positions of the polariser, analyser, and plate of quartz.

I also made a number of measurements of the larger rings in Plate 1, but these, I regret to say, have proved to be useless. The formulæ, which are compact enough when the plate is cut truly perpendicular to the axis, become hopelessly complicated when the deviation of the axis has to be introduced. Since the deviation of the axis was small I tried approximations, carrying them as far as the squares of the deviations in the two directions. But the discrepancy between the results for plane A and for plane B seemed to indicate that the cubes also should have been included.

I then determined to obtain a new plate in which the deviation of the axis should be negligibly small. I selected a good piece at HILGER's and got him to cut it roughly at right angles to the axis. I then set it up on the spectrometer, determined the magnitude and direction of the error, and sent it back to HILGER to be recut. By repeating this process, getting it recut no less than four times, I at length attained my object. This plate I will call Plate 2. It was perfectly clear and free from maccling. The two polished faces were good planes about 30 mm. square, and inclined at an angle of about 1½′. The two planes through the normal and parallel to the sides of the square I will call plane A and plane B. The error of the axis was about 6′ parallel to plane A and about the same parallel to plane B. This I found was small enough to be negligible throughout. The thickness was about 20 mm. only.

The first ring had nearly the same diameter as in Plate 1, but it was produced by a retardation of three wave-lengths instead of four. Owing to the smaller thickness the bands were broader and further apart than before; but I do not think this impaired the accuracy of measurement except perhaps slightly in the first two rings. I had the plate cut down to this thickness in order to secure good observations at the high angles of incidence. The object glasses of the telescope and collimator were barely 25 mm. in diameter, yet I was able to obtain good readings for the 150th ring at an angle of incidence of over 74°, which would have been quite impossible with a plate 25 mm. thick.

The observations on the small rings in Plate 2 were similar to those in Plate 1, except that three readings were taken throughout for each side of the first ring and two readings for each side of the second ring. The greatest difference between the readings was $1\frac{1}{2}'$ in the first ring and $1'$ in the second. As will be seen below the first ring gave results which were at first sight rather discordant with the others. So I made a few special observations on the first ring with a very bright sodium-flame. This was obtained, without the use of oxygen, with the aid of a thin platinum wire carrying a very small bead of carbonate of sodium. The thin wire was raised to an intense heat in the hottest part of the flame, while sufficient liquid oozed down the wire from the molten bead to replace the sodium given off. The flame was nearly if not quite as bright as if oxygen had been blown in, and the definition of the first ring was decidedly improved; though traces of other colours appeared which were a little troublesome.

The measurements of the larger rings deserve a few remarks. The rings were narrow and sharply defined, so the needle-point, could be placed with great accuracy, and another important source of error was removed, for turning the polariser or analyser slightly would not appreciably displace the ring. I believe the discrepancies between different measurements that appear in the tables arose chiefly from errors of $\frac{1}{2}'$ in reading the verniers. Owing to the lateral displacement of the light when the plate was placed obliquely, the telescope had to be moved various distances up to about 1° to either side of its mean position. To make allowance for this motion the telescope vernier had to be read. Thus each diameter given depends on four vernier readings. It is not then very surprising that two diameters should occasionally differ by $1\frac{1}{2}'$; while the mean of the four diameters is probably very accurate.

The patch of light alluded to previously as forming the field of view was, as the angle of incidence increased, gradually encroached on by the edge of the object-glass of the telescope. This was avoided by moving the telescope. But soon the edges of the quartz plate began to encroach, and this was unavoidable. When the 150th ring was on the needle-point the field of view was very narrow, so the readings were not quite as accurate as for the other rings. Still I do not think the error of setting the needle-point was ever as much as $1'$. Notwithstanding the movement of the telescope the light at the high angles of incidence entered near the edge of the object-glass; so I carefully tested the telescope for spherical aberration and found that no appreciable error could arise from this cause. As a matter of curiosity I found it was possible to obtain a reading of both sides of the 163rd ring.

The above observations relate to values of ϕ ranging from 4° to 38°. For larger values I required a plate cut parallel to the axis. So I had two new faces cut on Plate 2, at right angles to the former ones and therefore nearly parallel to the axis, forming in fact a new plate, which I will call Plate 3. The two new faces were good planes and made an angle of about $2\frac{1}{2}'$ with one another, and not more than $9'$ with the axis.

In the observations on Plate 3, it was necessary to set all four faces nearly parallel to the axis of rotation of the spectrometer table so as to secure that the axis should lie in the plane of measurement. The bands were shadowy and indistinct compared with those seen in Plate 2. This was only to be expected, for we really have two distinct sets of bands due to the two sodium lines. For a given value of ϕ the retardation is very nearly the same for either line, but if it amounts to 300 wave-lengths for D_1 it will be about 300·3 wave-lengths for D_2. Thus the 300th band for D_1 will divide the distance between the 300th and 301st bands for D_2 in the ratio of 3 to 7, now in the bands observed the retardation ranged from 253 wave-lengths to 312. So it was no wonder the bands were indistinct, the wonder was rather that they were measurable at all. Fortunately however a large angular error in the measurement of a band only produced a small error in the retardation deduced. To take an extreme example, in the first band an error of $10'$ in the diameter only produced an error of $\frac{1}{10000}$th part in the retardation deduced therefrom. I took two sets of measurements of these bands with the analyser in one position and two sets with it in the rectangular position. The 2nd, 5th, 15th, 30th, and 50th bands were measured in all four sets, the first only in the first set, and the 60th only in the two last. On either side of the first band I took three readings, the extreme difference between two being $14'$. For the second I usually took two readings, the extreme difference in one case being $9'$, the next greatest being $5\frac{1}{2}'$. For the fifth in four cases I took two readings, the extreme difference being $2\frac{1}{2}'$. But, as will be seen below, these differences are quite eclipsed by those due to small differences of temperature on different days.

Indeed if it was desired to get a very accurate measure of the change of $a-b$ with temperature a most powerful method would be to take similar observations to these, using a plate of quartz about 70 mm. thick, so that the bands for the two D lines would nearly overlap, and thus narrow and sharply-defined bands would be presented in the field of view.

The Measurement of the Thickness.

The thickness of the plates was measured with a pair of callipers made by Elliott Bros. These were fitted with a vernier reading to thousandths of an inch, and the graduation was so good that it was easy to divide the vernier divisions into halves or even quarters. To avoid any error arising from the jaw faces of the callipers not being strictly plane, I clamped two pins on to the jaws of the callipers with their heads opposed to one another. The direct contact of the two pins' heads was observed with a magnifying glass, and when the quartz was interposed each pin's head was brought up into contact with its image in the surface of the quartz. Care was of course taken to set the plate of quartz at right angles to the length of the callipers. This gave the thickness of Plate 1, 1·0885 inch or 27·65 mm., of Plate 2, ·7865 inch or 19·977 mm.

These are probably correct within $\frac{1}{2000}$th inch. If I had measured Plate 3 in the same way I might have got an error of $\frac{1}{1000}$th part in the ratio of its thickness to that of Plate 2. Now it was the ratio that I was anxious to get accurately, for, as will appear below, I was more interested to see whether $a-b$ would come out from my calculation a constant, than to find out what might be the value of that constant. I had arranged that Plate 3 should be of nearly the same thickness as Plate 2. If then I could get an accurate value of the difference between them, it would supply an accurate value of the ratio. This difference was measured with a spherometer reading to ·001 mm. The plate was laid on three steel points firmly fixed into a table. The three legs of the spherometer rested on a mahogany block clamped to the table. Each leg had been pressed gently into the wood to make a small pit, and I found that the spherometer could be lifted off and replaced several times, and yet give the same reading. I found the difference of thickness to be ·275 mm. within ·002 mm. Thus I obtained the ratio correct to $\frac{1}{10000}$th part.

III.—Calculation and Discussion of Results.

It is convenient to discuss the observations on small values of ϕ separately from the others. Near the optic axis the additional separation of the sheets of the wave-surface, due to the rotatory property, has to be treated as of magnitude comparable with the separation given by Huyghens' construction, both being very small. While at a little distance from the axis the Huyghenian separation is greatly increased, and the additional portion sinks to the magnitude of a small correction. Thus for each case a special formula of approximation is appropriate. The boundary may be drawn at $\phi=12°$, though either formula will do for some distance on either side of this boundary.

The Small Rings.

In my former paper I calculated the radii of the various small rings on MacCullagh's theory and compared their values with observation. In order to compare the observations with other theories the results will now be presented in a different form, and it is convenient to introduce a quantity D to denote the number of wave-lengths by which one wave lags behind the other in air after the light has traversed normally a plate of quartz 1 mm. thick, the normal to whose faces makes an angle ϕ with the optic axis. Let R denote the retardation actually observed when the light passes obliquely through the plate. We have to determine the relation between R and D. If we were free to assume that the two wave-fronts in the crystal might be treated as parallel this would be very simple, and in my former paper I made this assumption; but further consideration has convinced me that the assumption is inadmissible, at any rate without a good deal more explanation. It is true that the two wave-fronts are very nearly parallel, but it is also true that the retardation to be measured depends on the small difference between two nearly equal velocities. I therefore give the following more rigorous investigation, which leads, as will be seen, to the same result as the questionable assumption.

Fig. 2.

Let FGC in fig. 2 represent a plate of quartz. Let ABCD be a wave-front; of which the part AB has not reached the quartz, and the part BC is an "ordinary" wave-front in the crystal. Let ι be the angle of incidence, ι' ι'' the two angles of refraction.

Then the retardation of the ordinary wave in passing through the plate is the perpendicular distance between CD and ABE

$$= \mathrm{T}\frac{\sin(\iota-\iota')}{\sin\iota'} = \mathrm{T}(\sin\iota\cot\iota' - \cos\iota).$$

Similarly the retardation of the extraordinary wave is

$$\mathrm{T}(\sin\iota\cot\iota'' - \cos\iota).$$

So the relative retardation is

$$\mathrm{T}\sin\iota\,(\cot\iota'' - \cot\iota') \quad . \quad . \quad . \quad . \quad (1)$$

This is a well-known result, the above proof being due to Dr. ROUTH. I have inserted it for the sake of completeness, and to show that so far no approximations have been made.

Let s' s'' be the two wave-velocities in the quartz, then

$$\left.\begin{aligned}\sin \iota' &= s' \sin \iota\\ \sin \iota'' &= s'' \sin \iota\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

Let

$$s''=s'-\sigma, \qquad \iota''=\iota'-\epsilon.$$

We shall see that σ/s' is always less than $\frac{1}{1500}$, so that although R contains σ as a factor the squares of σ/s' may be neglected, while ϵ/ι' is smaller still.

From (2) we obtain

$$\epsilon \cos \iota' = \sigma \sin \iota.$$

Then

$$\cot \iota'' - \cot \iota' = \frac{\epsilon}{\sin^2 \iota'} = \frac{\epsilon}{s'^2 \sin^2 \iota} = \frac{\sigma}{s'^2 \sin \iota \cos \iota'}$$

Whence

$$R = T \sin \iota\, (\cot \iota'' - \cot \iota') = \frac{T\sigma}{s'^2 \cos \iota'}$$

Again

$$D\lambda = \frac{1}{s''} - \frac{1}{s'} = \frac{\sigma}{s'^2} = \frac{R \cos \iota'}{T}$$

I have examined the effect of retaining the squares of σ and ϵ in finding this relation, and find that the above equation is true within one part in ten thousand.

For the successive rings we have $R=n\lambda$, where n is an integer.

So

$$D = \frac{n \cos \iota'}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where T is measured in millimetres.

All the nine theoretical formulæ I have examined for the relative retardation near the axis in quartz take one or other of the following forms:—

$$\left.\begin{aligned} &D^2 = P_1^2 \sin^4 \phi + D_0^2\\ \text{or}\quad &D^2 = P_2^2 \sin^4 \phi + D_0^2 \cos^4 \phi\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where P_1 and P_2 are constants which have certain values assigned to them.

D_0 is the value of D when $\phi=0$, and is known from the rotation. If ρ be the rotation, measured in degrees, of a millimetre plate of quartz $\rho=180D_0$.

If the plate be cut strictly at right angles to the optic axis $\phi=\iota'$ and the diameter of each ring is 2ι. Using the equation $\sin \phi = a \sin \iota$, where $1/a$ is the ordinary index, and eliminating D between (3) and (4) we have

$$n^2 \cos^2 \phi = T^2 (P_1^2 a^4 \sin^4 \iota + D_0^2)$$
$$n^2 \cos^2 \phi = T^2 (P_2^2 a^4 \sin^4 \iota + D_0^2 \cos^4 \phi)$$

Thus, from the observed values of ι, we can obtain values of P_1 and P_2 for each ring. According to one set of theories P_1, according to the other P_2 should be always the same.

The observations on Plate 1 are exhibited in Table I. The first line gives the value of n; the next four the observed values of the diameters taken in plane A or in plane B with the principal plane of the analyser in the position indicated; the sixth line the result of taking the mean of the two diameters in plane A and correcting it for the deviation of the axis from the normal; the seventh the same for plane B; the eighth the mean of the two last. The ninth shows the diminution of P_1 or P_2 for an increase of 1′ in the diameter, so as to give an indication of the probable accuracy. The next line gives the approximate value of ϕ, and the last two the values of P_1 and P_2 deduced from each ring.

TABLE I. (Plate 1).

Temp.	Value of *n*.	4.	5.	6.	7.	8.	13.	18.
19½°	Plane A analyser ╲ . .	12° 49½′	16° 39′	19° 17′	21° 25½′	23° 16¾′	30° 40′	36° 27′
15¼°	" " ╱ . .	12° 48½′	16° 37′	19° 15½′	21° 24½′	23° 17′	30° 38½′	36° 26′
13½°	Plane B " ╲ . .	12° 52′	16° 41′	19° 17½′	21° 25½′	23° 17½′	30° 38½′	36° 25′
14½°	" " ╱ . .	12° 51′	16° 40½′	19° 17′	21° 24¾′	23° 17½′	30° 37½′	36° 25′
	Corrected mean plane A .	12° 50½′	16° 39′	19° 16¾′	21° 25′	23° 17′	30° 38½′	36° 25′
	" " " B .	12° 52′	16° 41¼′	19° 17½′	21° 25½′	23° 18′	30° 38½′	36° 25½′
16°	Mean corrected diameter .	12° 51¼′	16° 40′	19° 17′	21° 25¼′	23° 17½′	30° 38½′	36° 25¼′
	Change of P_1 or P_2 per 1′ in diameter	·040	·030	·026	·024	·022	·0165	·014
	Approximate ϕ	4° 9′	5° 23′	6° 14′	6° 55′	7° 31′	9° 51′	11° 40′
	" P_1	15·084	15·181	15·204	15·221	15·232	15·272	15·285
	" P_2	15·258	15·290	15·295	15·297	15·290	15·309	15·309

The observations on the small rings of Plate 2 are exhibited in Table II.

TABLE II. (Plate 2).

Temp.	Value of *n*,	3,	4.	5.	6.	7.	9.	13.
22°	Plane A analyser ╱ . .	13° 38¾′	18° 10′	21° 16½′	23° 48½′	26° 5′	29° 58½′	36° 26½′
21°	" " ╲ . .	13° 36½′	18° 8½′	21° 15′	23° 48½′	26° 3½′	29° 56½′	36° 26½′
18°	Plane B " ╱ . .	13° 34½′	18° 7¾′	21° 14½′	23° 48′	26° 3′	29° 56½′	36° 25½′
22°	" " ╲ . .	13° 37′	18° 10½′	21° 16′	23° 49½′	26° 3′	29° 57′	36° 26′
20¾°	Mean diameter	13° 36½′	18° 9¼′	21° 15½′	23° 48½′	26° 3½′	29° 57′	36° 26′
	Approximate ϕ	4° 24′	5° 51½′	6° 51½′	7° 40½′	8° 23½′	9° 38′	11° 41′
	" P_1	15·054	15·207	15·220	15·260	15·249	15·258	15·269
	" P_2	15·220	15·293	15·290	15·311	15·295	15·292	15·292

On looking at these tables we see that P_1 gives values steadily increasing with ϕ, while P_2 remains very nearly the same throughout. I think that the final values of the diameters of the four larger rings in each table should be correct within ½′ or ¾′, while the first three should not be in error more than 1′. In Table I. there is a line indicating the change in P_1 or P_2 corresponding to 1′ in the diameter. So we see that P_2 comes out as a constant within the limits of experimental error except for the first ring in Plate 2. It was for this reason that I made a special set of measurements of the first ring in Plate 2 with a very bright light. The values obtained in three different positions of the analyser and plate were 13° 36$\frac{3}{4}$′, 13° 34$\frac{3}{4}$′, and 13° 37′, mean 13° 36′, mean temperature 22$\frac{1}{2}$°. This gives precisely the same value, 15·220. Plate 1 also gives a decided drop in P_2 for the first ring which is barely within the limits of error above assigned. Now a change of $\frac{1}{1000}$th in the value of ρ employed in the calculation would alter P_2 by ·0275 for the first ring in Plate 2, and by ·0344 for the first ring in Plate 1. Thus a decrease of two parts in the thousand in the value of the rotation would bring the deviation of P_2 from the constant value well within the limits of error. The other rings are much less dependent on ρ; thus the same change in ρ would in the second ring only increase P_2 by ·0086. The most extended observations on the rotation are those of **Soret** and **Sarasin** ('Comptes Rendus,' tome 95 (1882), pp. 635–638, &c.). By the method of **Fizeau** and **Foucault** they obtain for D_1 21·73°, for D_2 21·69°, mean 21·71°; while by direct observation with sodium light they obtain 21·73°. I have calculated from the mean of these 21·72, applying the temperature correction which is an addition of ·00324 for each degree rise of temperature. The deduction of two parts in a thousand will bring the value down to 21·68°. Another, and, in my opinion, better explanation of the peculiar result from the first ring will be given later on.

Omitting the first ring my observations give P_2 a constant value of 15·30±·01. We have to examine how this agrees with the values assigned by the theories.

Cauchy gives

$$P_2=\frac{a-b}{a^2\lambda}=15{\cdot}351$$

where a and b are the wave-velocities at right angles to the axis.

Lommel gives

$$P_2=\frac{1-a^2}{1-b^2}\,\frac{a+b}{2a}\,\frac{a-b}{a^2\lambda}=15{\cdot}178\,;$$

Kettler gives

$$P_2=\frac{a+b}{2b}\,\frac{a-b}{a^2\lambda}=15{\cdot}486\,;$$

Sarrau gives

$$P_2=\frac{a+b}{2a}\,\frac{a-b}{a^2\lambda}=15{\cdot}306.$$

The discrepancy between **Cauchy's** value and the observed value is outside any probable errors of observation. It corresponds to a change of 4′ in the diameter of the 7th and 11th rings. Such an error seems out of the question. **Lommel** and

Kettler are still further from the truth. The other five, MacCullagh, Clebsch, Lang, Boussinesq, and Voigt have the first form of expression, giving

$$P_1 = \frac{a+b}{2a}\,\frac{a-b}{a^2\lambda} = 15{\cdot}306.$$

Thus Sarrau alone succeeds in explaining the observations satisfactorily, though Voigt does put in a proviso that his D_0 may vary with ϕ.

In obtaining the above figures the difficulty arose that $a-b$ was known only roughly from spectrometer observations. I have, therefore, had to use the value of $a-b$ deduced on Sarrau's or MacCullagh's theories from the observations on the very large values of ϕ, viz., $a-b = {\cdot}003793 \pm {\cdot}000002$.* It might perhaps be objected that it is not fair to test one theory with the value of constant obtained from another. But it should be remembered that the separation between the two sheets changes very slowly with ϕ when ϕ is nearly 90°, and that I have obtained a measurement for $\phi = 85° \; 37'$. Thus on any theory I should have obtained much the same value of $a-b$ from this measurement.

Of the above writers Cauchy, Lommel, and Lang give the actual expressions I have quoted. The others only give equations to the wave-surface, from which I have had to deduce the expressions given above. MacCullagh, Clebsch, Lang, Boussinesq, and Voigt all give the same wave-surface, viz.,

$$(s^2-a^2)(s^2-a^2\cos^2\phi-b^2\sin^2\phi)=q^2$$

where q is a constant depending on the rotatory power. Sarrau's wave-surface, neglecting certain constants, f_1 and g_1, which he says are probably small, is

$$(s^2-a^2)(s^2-a^2\cos^2\phi-b^2\sin^2\phi)=q^2\cos^4\phi.$$

Thus these six theories agree with the Huyghenian construction when the rotatory term is neglected. This is *à priori* a great point in their favour, since we know from Stokes's and Glazebrook's observations that in Iceland Spar the Huyghenian construction is a very close approximation to the truth.

The more complete form of Sarrau's wave-surface will be examined towards the end of the paper.

The references are as follows :—

MacCullagh, Trans. Roy. Ir. Acad., vol. 17 (1837), p. 463.

Cauchy, Ann. de Chim. et de Phys., sér. 3, tome 30 (1850), p. 68 ; a paper by Jamin.

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* A better value is ·0037945 ± ·0000005, which gives for Sarrau $P_2 = 15{\cdot}312 \pm {\cdot}002$. Thus, though Sarrau's formula agrees with observation much better than any of the others, there is a small outstanding discrepancy in the three larger rings in Table II., which is as hard to account for by errors of observation, as the great drop in the first ring. This is discussed, and an explanation given near the end of the paper.—[May 31, 1886.]

Clebsch, 'Crelle's Journal,' band 57 (1859), p. 356.
Sarrau, Liouville, sér. 2, tome 13 (1868), p. 101.
Boussinesq, Liouville, sér. 2, tome 3 (1868), p. 335.
Lang, Pogg. Ann. Ergbd., band 8 (1878), p. 622.
Lommel, Wied. Ann., band 15 (1882), p. 389.
Kettler, Wied. Ann., band 16 (1882), p. 109.
Voigt, Wied. Ann., band 19 (1883), p. 898.

For some account of most of these theories see Glazebrook's 'Report on Physical Optics,' Brit. Assoc., 1885.

Corrections for error of axis in Plate 1.

The calculations were made as though the optic axis were coincident with the normal to the faces. To compensate for this certain small corrections have to be applied to the observed diameters. The error parallel to plane A was 1° 45′, parallel to plane B 18′. First consider the measurements in plane A, and take the error $\alpha=1^\circ\,45'$ by itself. It is clear that we may calculate what the error would be, on the assumption that MacCullagh's theory were true, for any value of ϕ which is near the true value, and take this with sufficient accuracy to be the actual error on any one of the theories.

Let $\phi=\phi_1$ give a band on one side. The angle of refraction is then $\phi_1-\alpha$, so we have

$$\frac{n^2\cos^2(\phi_1-\alpha)}{T^2}=P_1^{\,2}\sin^4\phi_1+D_0^{\,2}$$

Solving we get ϕ_1, and from the equation $\sin(\phi_1-\alpha)=a\sin\iota_1$ we obtain ι_1, the angle of incidence on that side.

Similarly, putting α for $-\alpha$ we obtain ι_2 the angle of incidence on the other side. The observed diameter is then $\iota_1+\iota_2$, and we take ϕ_3 to be the value of ϕ which would give the dark band in a piece correctly cut, where $\sin\phi_3=a\sin\frac{\iota_1+\iota_2}{2}$. But the true value is ϕ_4 where

$$\frac{n^2\cos^2\phi_4}{T^2}=P_1^{\,2}\sin^4\phi_4+D_0^{\,2}$$

By calculating ϕ_3 and ϕ_4 we obtain the proper correction to apply to ϕ_3, and therefore to the observed diameter. In practice I found that the correction could be obtained with sufficient accuracy on the assumption that $\phi_1=\phi_2=\phi_4$.

On this score I had to subtract from the observed diameters of the successive rings

$$\tfrac{1}{2}'\quad\tfrac{1}{2}'\quad\tfrac{3}{4}'\quad 1'\quad 1'\quad 1\tfrac{1}{2}'\quad 2'$$

Again the axis lay 18′ above the plane of measurement, so a chord of the circular ring was measured instead of the full diameter. On this score the following corrections had to be added

$$2' \quad 1\tfrac{1}{2}' \quad 1\tfrac{1}{4}' \quad 1' \quad 1' \quad \tfrac{3}{4}' \quad \tfrac{1}{2}'$$

On the whole I had to add

$$1\tfrac{1}{2}' \quad 1' \quad \tfrac{1}{2}' \quad 0' \quad 0' \quad -\tfrac{3}{4}' \quad -1\tfrac{1}{2}'$$

Secondly, for the measurements in plane B.

Now $\alpha=18'$ only, so the corrections on this score are negligible. In this case the plate was tilted till the apparent position of the axis in air lay in the plane of measurement. So ι was no longer the radius of the rings in air and ι' consequently had to be altered. To allow for this I had to add to the successive diameters

$$\tfrac{1}{2}' \quad \tfrac{1}{3}' \quad \tfrac{1}{3}' \quad \tfrac{1}{3}' \quad \tfrac{1}{3}' \quad \tfrac{1}{3}' \quad \tfrac{1}{2}'$$

The corresponding corrections for Plate 2 would be infinitesimal.

The Large Rings.

Since MacCullagh's theory will be found to be in tolerable agreement with the measurements obtained for the larger values of ϕ, it is convenient to take it as a basis and discuss later what modifications would make the agreement more perfect.

MacCullagh starts by assuming the equations of motion

$$\left.\begin{aligned}\frac{d^2\xi}{dt^2}&=\mathrm{A}\,\frac{d^2\xi}{dz^2}+\mathrm{C}\,\frac{d^3\eta}{dz^3}\\ \frac{d^2\eta}{dt^2}&=\mathrm{B}\,\frac{d^2\eta}{dz^2}-\mathrm{C}\,\frac{d^3\eta}{dz^3}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (5)$$

where ξ, η are the displacements parallel to x, y at any time t, and the axis of z is the wave normal.

Also

$$\left.\begin{aligned}\mathrm{A}&=a^2\\ \mathrm{B}&=a^2\cos^2\phi+b^2\sin^2\phi\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (6)$$

C is a constant.

From these equations we get the wave-surface

$$(s^2-\mathrm{A})(s^2-\mathrm{B})=\frac{4\pi^2\mathrm{C}^2}{s^2\lambda^2} \quad \ldots\ldots\ldots\ldots \quad (7)$$

which has three sheets; the third sheet, however, corresponds to an index of refraction of about 40,000; so for physical purposes we need not consider it.

Now we shall find the whole effect of C^2 is so small, not exceeding $\frac{1}{150}$th part of the chief terms in the final formula, that we may not merely reject its squares but also put $B=a^2$ in the small terms, except, of course, in the factor $B-a^2$ itself.

Resuming the rotation used for the smaller rings we have

$$\left.\begin{aligned} s'^2&=a^2+\frac{4\pi^2C^2}{a^2\lambda^2(a^2-B)} \\ s''^2&=B+\frac{4\pi^2C^2}{B\lambda^2(B-a^2)} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\sin\iota'=s'\sin\iota, \qquad \sin\iota''=s''\sin\iota.$$

By equation (1) the retardation R is

$$T\sin\iota\,(\cot\iota''-\cot\iota')$$

Assuming that the normal to the plate coincides with the optic axis we have for the ordinary wave

$$B=a^2\cos^2\iota'+b^2\sin^2\iota'$$

So $a^2-B=(a^2-b^2)\sin^2\iota'=(a^2-b^2)a^2\sin^2\iota$, neglecting C.

For the extraordinary wave

$$B=a^2\cos^2\iota''+b^2\sin^2\iota'', \qquad a^2-B=(a^2-b^2)\sin^2\iota''=(a^2-b^2)a^2\sin^2\iota,$$

with sufficient accuracy. Hence

$$\left.\begin{aligned} s'^2&=a^2+K \\ s''^2&=B-K \end{aligned}\right\}$$

where

$$K=\frac{4\pi^2C^2}{a^4\lambda^2(a^2-b^2)\sin^2\iota}.$$

To obtain the part of R not involving C we have

$$\begin{aligned} \sin^2\iota''&=B\sin^2\iota \\ &=(a^2\cos^2\iota''+b^2\sin^2\iota'')\sin^2\iota\,; \end{aligned}$$

therefore

$$\cot\iota''=\frac{\sqrt{1-b^2\sin^2\iota}}{a\sin\iota}.$$

Similarly

$$\cot\iota'=\frac{\sqrt{1-a^2\sin^2\iota}}{a\sin\iota}\,;$$

therefore

$$\mathrm{R}=\frac{\mathrm{T}}{a}\left(\sqrt{1-b^2\sin\iota}-\sqrt{1-a^2\sin^2\iota}\right)$$

$$+\text{ a term involving C.}$$

This term

$$=\mathrm{T}\sin\iota\left(\frac{d\cot\iota''}{d\mathrm{K}}-\frac{d\cot\iota'}{d\mathrm{K}}\right)\mathrm{K},$$

where K is to be put zero in each differential coefficient after differentiation.

$$\frac{d\cot\iota''}{d\mathrm{K}}=-\frac{1}{\sin^2\iota''}\frac{d\iota''}{d\mathrm{K}}=-\frac{1}{a^2\sin^2\iota}\frac{d\iota''}{d\mathrm{K}}$$

and

$$\sin^2\iota''=(a^2-\mathrm{K})\sin^2\iota$$

$$\sin 2\iota''\frac{d\iota''}{d\mathrm{K}}=-\sin^2\iota$$

therefore

$$\frac{d\cot\iota''}{d\mathrm{K}}=\frac{1}{a^2\sin 2\iota''}=\frac{1}{2a^3\sin\iota\sqrt{1-a^2\sin^2\iota}}$$

Similarly

$$\frac{d\cot\iota'}{d\mathrm{K}}=-\frac{1}{2a^3\sin\iota\sqrt{1-a^2\sin^2\iota}}$$

therefore

$$\mathrm{R}=\frac{\mathrm{T}}{a}\left(\sqrt{1-b^2\sin^2\iota}-\sqrt{1-a^2\sin^2\iota}\right)$$

$$+\frac{4\pi^2\mathrm{C}^2\mathrm{T}}{a^4\lambda^2(a^2-b^2)\sin^2\iota}\;\frac{1}{a^3\sqrt{1-a^2\sin^2\iota}}\quad\ldots\ldots\ldots\quad(9)$$

This equation is not true for small values of ι or ϕ, for we have assumed in the course of the proof that K is small. We cannot, therefore, put $\phi=0$ and obtain R_0 from (9), but by putting $\phi=0$ in (7) we obtain

$$\frac{\rho}{180}=\frac{1}{s'\lambda}-\frac{1}{s\lambda}=\frac{2\pi\mathrm{C}}{a^4\lambda^2}\quad\ldots\ldots\ldots\quad(10)$$

Equation (9) is not convenient for calculation, for each of the radicles in the bracket is very large compared with their difference. And it is on their difference that R depends. Remembering that $\mathrm{R}=n\lambda$, we may put (9) into the form

$$\frac{(a-b)(a+b)\sin^2\iota}{\sqrt{1-b^2\sin^2\iota}+\sqrt{1-a^2\sin^2\iota}}=\frac{an\lambda}{\mathrm{T}}-\frac{a^2\lambda^2}{a^2-b^2}\overline{\left.\frac{\rho}{180}\right|}^{2}\frac{1}{\sin^2\iota\sqrt{1-a^2\sin^2\iota}}\quad\ldots\quad(11)$$

Of the quantities involved in this equation a, b, and λ are known with great accuracy, certainly within one part in ten thousand. T also is known with considerable accuracy, but the value of $a-b$ is uncertain, to the extent of perhaps 1 per cent. The third term is small compared with the others, and so requires only approximate values of $a-b$ and c. We may therefore use (11) as an equation to find $a-b$, inserting the observed value of ι for each of the rings measured. If the value of $a-b$ does not come out the same for each ring, then MACCULLAGH's theory is inconsistent with the facts, unless indeed the discrepancies may be attributed to errors of observations.

This mode of presenting the results of the measurements possesses the great advantage that it shows at once how far the observed wave-surface departs from the theoretical one. For instance, if for a certain value of ϕ $a-b$ comes out $\frac{1}{1000}$th part too large, this indicates that the real separation of the two sheets is very approximately $\frac{1}{1000}$th part greater than that given by the theory. This is true throughout, except for the first two small rings.

The results from the large rings in Plate 2 are exhibited in Table III. The first line gives the value of n. The next four lines give the observed diameters, two sets of observations having been taken in plane A and two in plane B. The oblique strokes indicate the position of the principal plane of the analysing NICOL. To each set is attached the mean temperature at which it was taken. The sixth line gives the mean observed diameters. The seventh the values of $a-b$ deduced from MACCULLAGH's theory. The eighth the change in $a-b$, which would be produced by an error of 1′ in the measured diameter; in this, to save space, the first five ciphers after the decimal point are omitted. The ninth line gives the value of ϕ.

TABLE III. (Plate 2).

Temp.	Value of *n*.	22.	32.	52.	77.	102.	127.	152.
21¼°	Plane A analyser ╲ . .	47° 54′	58° 11½′	75° 13′	93° 26′	110° 23½′	127° 50½′	148° 50′
22¾°	" " ╱ . .	47° 53½′	58° 11½′	75° 14′	93° 25′	110° 23′	127° 50′	148° 51′
22½°	Plane B analyser ╲ . .	47° 53′	58° 10½′	75° 12½′	93° 25′	110° 23½′	127° 50′	148° 52½′
23°	" " ╱ . .	47° 53′	58° 10′	75° 13′	93° 24½′	110° 24′	127° 50′	148° 51½′
22½′	Mean diameter	47° 53¼′	58° 11′	75° 13′	93° 25′	110° 23½′	127° 50½′	148 51½′
	$a-b$ MACCULLAGH . . .	·0037884	·0037899	·0037913	·0037922	·0037931	·0037925	·0037931
	Change in $a-b$ per 1′ in diameter × 10^5 . . .	·247	·197	·142	·102	·075	·053	·033
	Approximate ϕ	15° 14′	18° 21′	23° 16½′	28° 7½′	32° 7′	35° 34′	38° 36′
	$a-b$ SARRAU	·0037916	·0037922	·0037927	·0037931	·0037939	·0037932	·0037936

The eighth line is an important one since the accuracy with which $a-b$ is determined varies so much. Thus, while an error of 1′ in the diameter of the 150th ring gives a change of one part in eleven thousand, the same error in the 20th ring gives a change of one part in fifteen hundred. To bring up the numbers in the seventh line to one constant value we shall have to suppose errors of 2′, 1½′, 1½′, and 1′ for $n=22$, 32, 52, and 77 respectively. But it is very improbable that the mean observed value of the diameter of any ring, except, perhaps, the 150th, is more than 1′ in error; so MACCULLAGH's theory must be condemned.

Now, the theory that explained the observations on the small rings most satisfactorily was that of SARRAU. His wave-surface may be obtained from MACCULLAGH's by making C vary as $\cos^2\phi$. So we must modify equation (11) by introducing the factor $\cos^4\phi$ into the third term. Calculating from the modified formula we obtain the numbers given in the tenth line of the table. The departures from constancy can now be explained by errors of less than 1′ in the ring diameters, yet the numbers still suggest a gradual rise of $a-b$ with ϕ. We shall return to this point in discussing the results from Plate 3.

The Bands in Plate 3.

As ϕ increases the correction due to the rotatory term becomes rapidly smaller. Thus for the 150th ring in Plate 2 the change in the deduced value of $a-b$, which would be made by simply calculating from the Huyghenian construction, would be only one part in five thousand, and it may be readily shown that in Plate 3 it would never exceed one part in ten thousand. These figures refer to MACCULLAGH's theory, and in SARRAU's expressions the rotatory term is smaller still. By neglecting this term the formulæ for Plate 3 are greatly simplified.

We have now

$$s'^2=a^2$$

$$s''^2=a^2\cos^2\phi+b^2\sin^2\phi.$$

Since the plate is cut parallel to the axis we have for the extraordinary wave

$$\phi+\iota''=90^\circ\,;$$

therefore

$$\sin^2\iota''=(a^2\sin^2\iota''+b^2\cos^2\iota'')\sin^2\iota$$

and

$$\cot\iota''=\frac{\sqrt{1-a^2\sin^2\iota}}{b\sin\iota}\,;$$

while

$$\cot\iota'=\frac{\sqrt{1-a^2\sin^2\iota}}{a\sin\iota}.$$

But

$$R=T\sin\iota\,(\cot\iota''-\cot\iota')\quad\text{and}\quad R=n\lambda$$

therefore

$$n\lambda=T\cos\iota'\left(\frac{1}{b}-\frac{1}{a}\right),$$

or

$$a-b=\frac{nab\lambda}{T\cos\iota'}\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(12)$$

In calculating from the observations ι was taken to be half the angular distance from any band on one side of the normal to the corresponding band on the other side. For convenience I will call this distance the diameter. Then ι' was deduced from ι by the relation $\sin \iota' = a \sin \iota$, and $a-b$ determined from the formula (12). But now the question occurs, what value must be given to n. In Plate 2 n was easily determined for the first ring, and therefore for all the rest, by a rough calculation from the known rotatory power. But in Plate 3 n is so large that tolerably accurate values of the constants are required to distinguish between one integer and the next. Indeed, without the observations on Plate 2, I should have been unable to decide between five or six different integers. However with the aid of these observations the difficulty disappears. Using the value $a-b=\cdot 0037935$ in equation (12) I obtained for the second band, reckoning from the normal, after correcting for temperature, $n=310\cdot 91$, so I concluded that the true value was 311.

Fig. 3.

Perhaps the best evidence on this point is supplied by the diagram, fig. 3. In this diagram the ordinates represent $a-b-\cdot 003780$, while the abscissæ are the values of ϕ. The small circles are got from SARRAU'S theory, the crosses from MACCULLAGH'S. For $\phi > 50^\circ$ where the two theories agree there are two lines of small circles. The upper line is obtained on the supposition that $n=311$ for the second band, the lower line on the supposition that $n=310$.

The diameters obtained in four sets of measurements are given in Table IV. The first line gives the number of the band reckoned from the normal. The seventh the resulting values of $a-b$, omitting the decimal point and two ciphers, and the eighth the change in $a-b$ corresponding to 10′ in the diameter, omitting the decimal point and five ciphers. This line shows that the large discrepancies between different measurements mean only very slight variations in $a-b$. They are no doubt due mainly to changes of temperature. The temperature of course varied one or two degrees during each set of observations, and no doubt the temperature of the quartz was slightly different from that of the thermometer. The ninth line gives the values of ϕ, and the tenth the values of $a-b$ corrected to the temperature $22\frac{1}{2}°$. This was the mean temperature of the measurements of the large rings in Plate 2. The correction to $a-b$ per degree of temperature is $-·000000415$. The last line gives the values of $a-b$, taken on the supposition that $n=310$ for the second band and corrected for temperature. We notice that the greatest difference between the numbers in the tenth line is ·0000006, being about one part in six thousand. This is a strong confirmation of the truth of the Huyghenian construction for the region far removed from the axis, extending as it does from $\phi=54°$ to $\phi=85°$. The mean is $a-b=·0037945$.

TABLE IV. (Plate 3).

Temp.	No. of Band.	1.	2.	5.	15.	30.	50.	60.
20°	Analyser /	13° 34′	19° 35′	31° 28′	56° 10½′	82° 25½′	113° 37′	: :
20°	„ ⟨	: :	19° 50½′	31° 42′	56° 14′	82° 27′	113° 35½′	: :
22°	„ \	: :	19° 13′	31° 25′	56° 5½′	82° 20½′	113° 29′	130° 35½′
21°	„ \	: :	19° 28′	31° 27′	56° 6′	82° 23′	113° 33′	130° 39½′
20¾°	Mean diameter	13° 34′	19° 31½′	31° 30½′	56° 9′	82° 24′	113° 33½′	130° 37½′
	$a-b$ omitting ·00	37954	37953	37950	37951	37952	37954	37953
	Change in $a-b$ per 10′ omitting ·00000	030	037	055	105	140	140	140
	Value of ϕ	85° 37′	83° 40′	79° 53′	72° 15′	64° 45′	57° 11′	53° 58′
	$a-b$ reduced to $22\frac{1}{2}°$ omitting ·00	37944	37946	37943	37944	37945	37947	37949
	$n=310$ for 2nd band	37823	37823	37820	37816	37811	37802	37804

Referring back to Table III. we see that the numbers given there deduced from SARRAU's theory are uniformly lower. This may be partly due to a wrong value of T, but, as I have said above, I do not think the error in the ratio of the values of T for the two plates exceeded 1 in 10,000. Moreover, SARRAU's $a-b$ diminishes steadily with ϕ throughout. This is very apparent in the following figures, which are obtained by grouping three or four rings together, allowing as a possible error from the mean the combined effect of $\frac{1}{2}°$ in temperature and $\frac{1}{2}'$ in diameter. In the case of the three small rings, the 2nd, 3rd, and 4th, $\frac{3}{4}'$ is allowed. In the case of the 1st $1'$.

From 7 bands	$\phi=90°$ to $53°$	$a-b$ lies between	·0037941	and ·0037949
4 rings	$\phi=39°$ to $26°$	„ „	·0037928	„ ·0037940
3 rings	$\phi=25°$ to $14°$	„ „	·0037910	„ ·0037934
3 rings	$\phi=13°$ to $8°$	„ „	·0037874	„ ·0037916

3 rings	$\phi=$ 8° to 6°	$a-b$ lies between	·0037860	and	·0037954
[1 ring	$\phi=$ 4° 24′	„ „	·0037620	„	·0037808

Taking into consideration the probable accuracy of the observations the discrepancy is about equally strongly marked in the case of the first ring and the three rings 13° to 8°, and to a minor degree in the case of some of the others. The observations on Plate 1 are not here included, as we do not know the ratio of the thickness of Plate 1 to that of Plate 3 with sufficient accuracy.*]

Up to this point we have been treating certain constants, f_1 and g_1, which appear in SARRAU'S expressions as negligibly small. We will now examine whether by the aid of these constants we can obtain a more satisfactory agreement with observation.

SARRAU'S wave-surface is given by

$$(s^2-a^2)(s^2-a^2\cos^2\phi-b^2\sin^2\phi)=\frac{4\pi^2a^2}{\lambda^2}(g_2\cos^2\phi+f_1\sin^2\phi)(g_2\cos^2\phi-g_1\sin^2\phi)$$

Putting $\phi=90°$, we obtain for the equatorial radii α and β.

$$(s^2-a^2)(s^2-b^2)=-\frac{4\pi^2a^2}{\lambda^2}f_1g_1.$$

We might treat this equation to the wave-surface exactly as we have treated the simpler one, and obtain values of $\alpha-\beta$ from the observations on the different values of ϕ. But it may be shown without difficulty that if we equate the values of $a-b$ previously found to

$$(\alpha-\beta)(1+k\cot^2\phi)$$

where

$$k=\frac{8\pi^2a^2}{\lambda^2}\frac{g_2(f_1-g_1)}{(a^2-b^2)^2}$$

we shall attain the same result. In this it is, of course, assumed that f_1 and g_1 are small.

I have found that a suitable value of k is $-$·000033. Using this value we obtain the following figures :—

$\phi=$90° to 53°	$\alpha-\beta$ lies between	·0037941	and	·0037949
39° to 26°	„ „	·0037931	„	·0037943
25° to 14°	„ „	·0037919	„	·0037943
13° to 8°	„ „	·0037914	„	·0037956
8° to 6°	„ „	·0037943	„	·0038037
4° 24′	„ „	·0037830	„	·0038018

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* Added May 31, 1886.

Thus the value ·0037913 falls within each pair of limits. The last line of each list gives the results from the first ring obtained with the use of **Soret** and **Sarasin's** value of the rotation. Thus the sudden drop of P_2 for the first ring, which was the most striking eccentricity of the observations on the small rings, is explained at once by the more general form of **Sarrau's** theory, without the necessity of assuming an error in the rotational coefficient.

Of course we have had to assign an arbitrary value to k. But the form of the correction, viz., $k \cot^2 \phi$, was fixed by the theory, and was exactly the form that was required, giving, as it does, the correction for $\phi = 4° \, 24'$ some thirty times as great as that for $\phi = 53°$.

We have now compared **Sarrau's** theory and the **MacCullagh** group of theories with observation for all our values of ϕ. With regard to the remaining three, **Cauchy** has given, so far as I know, no general expression for the wave-surface, while **Lommel** and **Kettler** are so widely at variance with the Huyghenian construction that I have not thought it worth while to make a detailed comparison.

I find, however, that the values of $a-b$ deduced on **Kettler's** theory from my observations would differ by about 3 parts in 1000 for $\phi = 60°$ and $\phi = 85°$, whereas according to the Huyghenian construction they agreed within 1 part in 6000.

We conclude, then, that out of the nine theories we have examined the only one which agrees with observation is that of **Sarrau**, and that to make the agreement as perfect as possible we must choose his constants, so that

$$8\pi^2 a^2 g_2 (g_1 - f_1) = \cdot 000033 (a^2 - b^2)^2 \lambda^2$$

or

$$g_1 - f_1 = 1 \cdot 07 \, g_2.$$

IV.—VALUES OF THE CONSTANTS EMPLOYED.

I have used **Rudberg's** values for a and b, viz.,

$$a = \cdot 647593$$
$$b = \cdot 643799.$$

Mascart gives

$$a = \cdot 647573$$
$$b = \cdot 643756$$

I have taken $\lambda = \cdot 00058920$ mm. This is the mean of **Ångstrom's** values for D_1 and D_2.

Fizeau has given coefficients of the expansion of quartz with temperature along the axis and at right angles to it. He also measured the change of a and b with temperature. These are so small as to be negligible in the present case except for the change of $a-b$. This has been specially investigated by DUFET who finds the change per degree $-\cdot000000415$.

The rotatory constant I have discussed at length above, in connexion with the small rings.

The thickness of Plate 1 was found to be 27·65 mms., of Plate 2 19·977 mms., while the ratio of Plate 3 to Plate 2 was 1·01377.

Plate 2 was cut from the same crystal of quartz as Plate 1.

The rotation of the plane of polarisation produced by either is related to the direction of the light as the rotation to the translation of a right-handed screw. Such is usually called left-handed quartz.

The observations were taken in the Cavendish Laboratory, Cambridge, during the months of March and June, 1885.

V.—PREVIOUS MEASUREMENTS.

The only previous measurements of the retardation in quartz with which I am acquainted are those of JAMIN in 1850 (Ann. de Chim., sér. 3, vol. 30, p. 68), those of HECHT (WIED. Ann., band 20 [1883], p. 426), and my own (Proc. Camb. Phil. Soc., vol. 5 [1883], p. 53).

JAMIN rotated the plate of quartz between two crossed NICOLS as I have done, but he used parallel light, taking the reading when the field of view appeared darkest. Most of the measurements agreed with CAUCHY'S theory within one part in thirty, though there were a few wider discrepancies. This he considered satisfactory agreement. He obtained similar results from another series of experiments in which the axis ratios were also involved.

HECHT'S method was not very dissimilar to that of JAMIN. There is an important oversight in his paper. In estimating the probable error of D he makes the tacit assumption that a certain quantity he calls ϕ is known accurately; while in fact the main part of the error results from the inaccuracy of this ϕ. Correcting this I obtain —using my own notation—for

$$\phi=2^\circ\ 22\cdot4' \qquad D=\cdot1224\ (\pm\cdot0006)$$

$$\phi=7^\circ\ 11\cdot4' \qquad D=\cdot2750\ (\pm\cdot009)$$

whence I deduce for the former $P_2=12\cdot72\pm1\cdot8$, for the latter $P_2=15\cdot82\pm\cdot57$.

The results obtained in my own earlier paper were vitiated, partly by the addition of some corrections founded on an erroneous argument, and partly by the bad faces of the plate examined. The argument was as follows.

The observations were made by bringing the cross wire up to the sensibly dark part of the band, first on one side, then on the other. Then I argued that I knew the position and breadth of the sensibly dark region of the band, but I did not know that by taking the middle of this I should obtain the darkest point. The distance from band to band becomes smaller as we go further from the axis, and I took as an approximation that the darkest point would divide the sensibly dark region in the same ratio as the band itself divides the distance between the two neighbouring bands. Here was the mistake. For the sensibly dark region is that part of the band where the intensity of the light falls below a certain fixed value, and the intensity of the light obviously varies approximately as the square of the small angular distance from the point of total extinction. It might then be expected that this darkest point would lie practically at the middle of the sensibly dark region. This opinion was confirmed by a closer examination, with the aid of Sir GEORGE AIRY'S formula, for the intensity of any point of the field.

By the removal of those corrections the discrepancies I obtained between theory and observation would be reduced one-half, and the remainder may be easily accounted for by the imperfection of the polished faces. I knew that the rings would not be much altered by curvature of the faces; for when the incidence is nearly normal, a slight deviation of the path through the quartz does not materially increase the length of the path, so I contented myself with noticing in the measurements with the callipers that the faces appeared tolerably parallel and plane. Lately, however, I examined the crystal again, and optical tests showed that the curvature of the faces was quite sufficient to explain the discrepancy of some 5′ between theory and observation.

VIII. *Description of Fossil Remains, including Foot-bones, of* Megalania prisca.—

Part IV.

By Sir RICHARD OWEN, *K.C.B., F.R.S., &c.*

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[PLATES 13–15.]

I HAVE been favoured to receive from my friend, Dr. GEORGE BENNETT, F.L.S., of Sydney, New South Wales, a further collection of fossil bones "from the Gowrie Creek, Darling Downs, Queensland." Their correspondence in mineralized condition and colour indicates, and a vertebra supports by its degree of resemblance to the subject[*] of Plate 34, in the "Philosophical Transactions" for 1880, their reference to *Megalania prisca.*

I subjoin figures of the vertebra of the natural size. The neural spine is represented by a ridge which slightly expands at the hind end, Plate 13, fig. 3, *ns*, where it has been broken and worn down; but, as a "spine," it has been smaller and shorter than in the vertebra compared (Phil. Trans., *ut supra*). The abraded base of the spine, *ns*, occupies one inch of the hinder part of the ridge, traversing the mid-line of the neural arch, its greatest breadth being half an inch.

The outer surface of all the prominences of this vertebra shows the effects of the attrition to which it has been subject from repeated rollings during the "freshets" of the river. A comparison of fig. 13, Plate 15, of the present fossil with fig. 2, Plate 35, of the 'Philosophical Transactions' for 1880, will show the minor length of the centrum in comparison with its breadth, a proportion which, with the reduced spine, bespeaks a sacral character, and suggests that the previously described vertebra may have come from the lumbar region. The "tranverse processes," *d*, *d*, which, on the sacral hypothesis, articulated with iliac elements of the pelvic arch, have been broken off or ground down to their basal origin. The articular surfaces of the centrum, *b*, *c*, figs. 1, 2, 4, Plate 13, are, as in fig. 1 of the Plate above cited, oblique from above downward and backward, in basal contour widely elliptical, that at the fore end of the centrum, *c*, being, according to the Saurian rule, concave, the opposite, hinder surface, *b*, convex.

The anterior outlet of the neural canal, Plate 13, fig. 2*a*, *n*, is tranversely oval, and the canal there is partially divided into three channels by a low sharp ridge extending from each side of the upper half of the canal wall, and by a mid-ridge from the floor of the canal. The breadth of this orifice is twice its vertical diameter. The posterior outlet, fig. 2, *n*, has reverse proportions; the vertical diameter is 13 millims., the transverse one 10 millims., the lateral ridges project from the middle of each side wall; a lower broader ridge rises from the middle of the floor, but subsides as it extends along the canal.

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[*] Now in the Museum of Natural History, Cromwell Road.

It may be objected that a supply of neural energy to the pair of hind-limbs would call for greater space to lodge the expanse of the supplying portion of the myelon; but, if the now nearest known ally of *Megalania*—to wit, the diminutive existing *Moloch* lizard of Australia—be a guide, reference to the figure of its skeleton in the 37th Plate of the Phil. Trans. for 1880, will not encourage such objection. The lower lateral divisions of the neural canal of the present fossil vertebra may have lodged the origins of the crural nerves. It seems, probable, from present experience, that complete restoration of the great land or fluviatile horned Saurian of Australia will be by piecework. The present vertebra, like the subject of Plate 34, *tom. cit.*, exceeds in size any such in the skeletons of the existing *Crocodilia* of the Australian rivers which have come under my examination.

The articular surfaces of the prezygapophyses, *z*, *z*, look obliquely upward, inward, and slightly backward; those of the postzygapophyses, *z'*, *z'*, with opposite aspects, have suffered abrasion of the hinder border. The broken and abraded surfaces of this much-rolled bone expose a close cancellous structure, and the degree of petrifaction gives the fossil a massive character and great weight.

The remains accompanying the above described vertebra are of a foot or feet of *Megalania;* as I cannot determine whether of a "fore" or "hind" limb I term them "metapodials."

I was puzzled for a time by the subject of figs. 5–8, Plate 14. A bone as broad as long by no means suggested a metacarpal or metatarsal one; yet it was associated with others of, unquestionably, a fore or a hind foot. Sufficient of the proximal articular surface, fig. 5, *a*, remained to show it to have been very slightly concave, and it was continuous, at right angles, with a narrow flattened facet, elongated in a fore-aft direction, fig. 8, *a*, indicative of a collateral bone. The distal joint, fig. 8, *c*, forming one of the angles of the triangular bone, was entire, and presented a convex condyle which bespoke its reception by the proximal articular cup of a toe-phalanx.

The unusual triangular shape of the present metapodial is due to an extension of the entire shaft from the side opposite to that which supports the surface, *a* in fig. 8, and gradually losing breadth as it approaches the distal condyle, *c*. Along one side of the flattened surface there extends a raised, rough, narrow tract, fig. 5, *d*, *f*, indicative of the insertion of a powerful muscle. A broader, oblique, roughened tract, near the middle of the opposite side of the shaft, fig. 7, *e*, gives a similar indication of muscular implantation.

The lateral production of the metapodial shaft gradually loses breadth and thickness, and terminates in an obtuse border, *d*, figs. 6, 7, which extends, with a slight convex curvature, to the distal condyle, *c*. The figs. 5–8 of this singular bone may dispense with further verbal description.

The subject of figs. 10, 11, 12, Plate 15, is a metapodial with the family characters of that of figs. 5–8, Plate 14. It is from the same locality, shows the same colours and mineralized condition, and a similar, though inferior, proximal expansion; but with extensions of the flattened articular surface on both right and left sides of the proximal end of the shaft, showing it to have been situated somewhere between the innermost and the outermost of the metapodial series. The length of this bone is 2 inches, 10 lines=73 millims.; its antero-posterior breadth at the proximal end is 28 millims.; the same distal breadth is 20 millims.; the tranverse proximal breadth is 20 millims., the same distal breadth is 28 millims. The distal articulation, *c*, is a hemispheroid condyle, with a prominence on each side of the base, for ligamentous attachment.

The subject of figs. 13, 14, is also a metapodial, with an antero-posterior expanse of the proximal half of the shaft greater in degree than in the foregoing specimen, but less, in comparison with the length of the bone, than is the expanse shown in figs. 5 and 7, Plate 14. The proximal articular surfaces, *a*, *b*, meet at an acute angle defining that end of the bone by a curved edge. The broader articular surface, fig. 13, *a*, is flat, the narrower one, fig. 14, *b*, is slightly convex. The expanse of the bone is from before backwards. The distal half of the shaft, above the condyle, is triedral. On the expanded part of the shaft is the oblong, smooth, seemingly articular surface, figs. 13, 14, *d*, which bends round an angle of the beginning of the contracted part of the shaft. Another oblong, smooth prominence, fig. 13, *e*, is defined upon the opposite side. Two facets of the contracted part of the shaft meet at an obtuse ridge which terminates in an oblong smooth protuberance, fig. 13, *f*. On the opposite side of the distal end is a well defined oval tract, fig. 14, *g*.

Of the phalanges I select a proximal, figs. 16, 17, and a distal or ungual, figs. 18, 19, specimen, figures of which, with those of the metapodial bones, may serve as guides in the recognition of similar evidences of the megalanian genus, and add to the knowledge of the geographical distribution in Australia of this remarkable reptilian form. The proximal phalanx, figs. 16, 17, continues the character of unusual breadth of the upper end; it gives transversely 35 millims., the antero-posterior diameter of the middle of the shaft being 12 millims. The proximal articular surface, fig. 17, *a*, is moderately concave, bounded on each side by a stout tuberosity. The distal trochlea, 20 millims. transversely by 10 millims., *c*, fig. 16, is feebly convex antero-posteriorly, more feebly concave transversely. It seems to have been a phalanx of a first or a fifth toe.

Ungual phalanges of the intervening toes have a deeper trochlear proximal joint, fig. 18, *a*; beyond this surface the bone is perforated by a transverse canal, *b*, the lower wall of which forms a cross bar, *c*, affording an insertional leverage to the flexor tendon. From each outlet of the canal a groove extends forward, subsiding at the roughened core of the claw. The metapodials of the chameleon approach in some proportions, though remotely, the megalanian peculiarities of the foot-bones, but a more close examination and extensive comparison of these parts of the reptilian skeleton are needed.

Description of the Plates.

PLATE 13.

Sacral Vertebra of *Megalania prisca.*

Fig. 1. Side view.
Fig. 2. Back view.
Fig. 3. Upper view.
Fig. 4. Under view.

PLATE 14.

Metapodial Bone.

Fig. 5. Front view.
Fig. 6. Upper view.
Fig. 7. Back view.
Fig. 8. Side view.

PLATE 15.

Metapodials and Phalanges.

Fig. 10. Side view.
Fig. 11. Front view.
Fig. 12. Upper view.
Fig. 13. Side view.
Fig. 14. Opposite side view.
Fig. 15. Proximal end.
Fig. 16. Back view of a proximal phalanx.
Fig. 17. Proximal end of the same.
Fig. 18. Side view of a distal phalanx.
Fig. 19. Upper view of the same.

All the figures are of the natural size.

IX. *Dynamo-Electric Machinery.*

By J. HOPKINSON, *M.A., D.Sc., F.R.S., and* E. HOPKINSON, *M.A., D.Sc.*

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[PLATES 16–20.*]

Theoretical Construction of Characteristic Curve.

OMITTING the inductive effects of the current in the armature itself, all the properties of a dynamo machine are most conveniently deduced from a statement of the relation between the magnetic field and the magnetising force required to produce that field, or, which comes to the same thing but more frequently used in practice, the relation between the electromotive force of the machine at a stated speed and the current around the magnets. This relation given, it is easy to deduce what the result will be in all employments of the machine whether as a motor or to produce a current through resistance, through an electric arc, or in charging accumulators; also the result of varying the winding of the machine whether in the armature or magnets. The proper independent variable to choose for discussing the effect of a dynamo machine is the current around the magnets, and the primary relation it is necessary to know concerning the machine is the relation of the electromotive force of the armature to the magnet current. This primary relation may be expressed by a curve (HOPKINSON, Mechan. Engin. Instit. Proc., 1879, pp. 246 *et seq.*, 1880, p. 266), now called the characteristic of the machine, and all consequences deduced therefrom graphically; or it may be expressed by stating the E.M.F. as an empirical function of the magnetising current. Many such empirical formulæ have been proposed; as an instance we may mention that known as FRÖHLICH'S, according to whom, if c be the current in the magnets, E the resulting E.M.F., $E=\frac{ac}{1+bc}$. For some machines this formula is said to express observed results fairly accurately, but in our experience it does not sufficiently approximate to a straight line in the part of the curve near the origin. The character of the error in FRÖHLICH'S formula is apparent by reference to Sheet I. (Plate 16), which gives a series of observations on a dynamo machine, and for comparison therewith a hyperbola F, drawn as favourably as possible to accord with the observations.* Such empirical formulæ possess no advantage over the graphical method aided by algebraic processes, and tend to mask much that is of importance.

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* Plates 19, 20 added Aug. 17.

One purpose of the present investigation is to give an approximately complete construction of the characteristic curve of a dynamo of given form from the ordinary laws of electro-magnetism and the known properties of iron, and to compare the result of such construction with the actual characteristic of the machine. The laws of electro-magnetism needed are simply (THOMSON, papers on 'Electrostatics and Magnetism;' MAXWELL, 'Electricity and Magnetism,' vol. 2, pp. 24, 26, and 143), (1) that the line integral of magnetic force around any closed curve, whether in iron, in air, or in both, is equal to $4\pi nc$ where c is the current passing through the closed curve, and n is the number of times it passes through; (2) the solenoidal condition for magnetic induction, that is, if the lines of force or of induction be supposed drawn, then the induction through any tube of induction is the same for every section. Regarding the iron itself, we require to know from experiments on the material in any shape the relation between a, the induction, and α, the magnetic force at any point; for convenience write $a=f^{-1}(\alpha)$, or $\alpha=f(a)$. From these premises, without any further assumption, it is easy to see that a sufficiently powerful and laborious analysis would be capable of deducing the characteristic of any dynamo to any desired degree of accuracy. This we do not attempt, as even, if successful, the analysis would not be likely to throw any useful light on the practical problem. We shall calculate the characteristic, first making certain assumptions to simplify matters. We shall next point out the nature of the errors introduced by these assumptions, and make certain small corrections in the method to account for these sources of error, merely proving that the amount of these corrections is probable or deducing it from a separate experiment, and again compare the theoretical and the actual characteristic.

First approximation.—Assume that by some miracle the tubes of magnetic induction are entirely confined to the iron excepting that they pass directly across from the bored faces of the pole-pieces to the cylindrical face of the armature core. This, we shall find, introduces minor sources of error, affecting different parts of the characteristic curve to a material extent. Let I be total induction through the armature, A_1 the area of section of the iron of the armature, l_1 the mean length of lines of force in the armature; A_2 the area of each of the two spaces between core of armature and the pole-pieces of the magnets, l_2 the distance between the core and the pole-piece;

[* Added Aug. 17.—That **FRÖHLICH's** formula cannot be a thoroughly satisfactory expression of the characteristic of a dynamo machine is evident from the consideration that E should simply change its sign with c, that is, be an odd function of c. There should be a point of inflexion in the characteristic curve at the origin. Another empirical formula $\frac{E}{a}=\tan^{-1}\frac{c}{b}$ is free from this objection, but still fails to fully represent the approximation of the curve to a straight line on either side of the origin, and it is equally uninstructive with any other purely empirical formula.]

A_3 the area of core of magnet, l_3 the total length of the magnets. All the tubes of induction which pass through the armature pass through the space A_2 and the magnet cores, and by our assumption there are no others. We now assume further that these tubes are uniformly distributed over these areas. The induction per square centimetre is then $\frac{I}{A_1}$ in the armature core, $\frac{I}{A_2}$ in the non-magnetic spaces, $\frac{I}{A_3}$ in the magnet cores; the corresponding magnetic forces per centimetre linear must be $f\left(\frac{I}{A_1}\right)$, $\frac{I}{A_2}$, $f\left(\frac{I}{A_3}\right)$. The line integral of magnetic force round a closed curve must be $l_1 f\left(\frac{I}{A_1}\right)+2l_2\frac{I}{A_2}+l_3 f\left(\frac{I}{A_3}\right)$. In this approximation we neglect the force required to magnetise pole-pieces and other parts not within the magnet coils to avoid complication. The equation of the characteristic curve is then $4\pi nc=l_1 f\left(\frac{I}{A_1}\right)+2l_2\frac{I}{A_2}+l_3 f\left(\frac{I}{A_3}\right)$. This curve is, of course, readily constructed graphically from the magnetic property of the material expressed by the curve $\alpha=f(a)$. In Sheet I. curve A represents $x=l_1 f\left(\frac{y}{A_1}\right)$, the straight line B $x=2l_2\frac{y}{A_2}$, curve C $x=l_3 f\left(\frac{y}{A_3}\right)$, and curve D the calculated characteristic. When we compare this with an actual characteristic E, we shall see that, broadly speaking, it deviates from truth in two respects: (1) it does not rise sufficiently rapidly at first; (2) it attains a higher maximum than is actually realised. Let us examine these errors in detail.

(1) The angle the characteristic makes with the axis of abscissæ near the origin is mainly determined by the line B. We have in fact a very considerable extension of the area of the field beyond that which lies under the bored face of the pole-piece. The following consideration will show that the extension may be considerable. Imagine an infinite plane slab, and parallel with it a second slab cut off by a second

Fig. 1.

plane making an angle α. We want a rough idea of the extension of the area between the plates by the spreading of the lines of induction beyond the boundary. We know that the actual extension of the area will be greater than we shall calculate it to be if we prescribe an arbitrary distribution of lines of force other than that which is consistent with LAPLACE's equation.

Assume, then, the lines of force to be segments of circles centre O, and straight lines perpendicular to OA. The induction along a line PQR will be $\frac{V}{(\pi-\alpha)x+t}$, V being difference of potential between the planes, and the added induction from OPB will be $\int_0^x \frac{V dx}{(\pi-\alpha)x+t} = \frac{V}{\pi-\alpha} \log \frac{(\pi-\alpha)x+t}{t}$. Thus if $\alpha = \frac{\pi}{2}$ we have for $x=t$, $2t$, &c.

x	$\frac{1}{\pi-\alpha} \log \frac{(\pi-\alpha)x+t}{t}$
t	·599
$2t$	·904
$3t$	1·109
$4t$	1·263
$5t$	1·387
$10t$	1·792

showing that the extension of the area of the field is likely to be considerable.

(2) The failure of the actual curve to reach the maximum indicated by approximate theory is because the theory assumes that all tubes of induction passing through the magnets pass also through the armature. Familiar observations round the pole pieces of the magnets show that this is not the case. If ν be the ratio of the total induction through the magnets to the induction in the armature we must, in our expression for the line integral of magnetising force, replace the term $f\left(\frac{I}{A_3}\right)$ by $f\left(\frac{\nu I}{A_3}\right)$; ν is not strictly a constant, as we shall see later; it is somewhat increased as I increases owing to magnetisation of the core of the armature, and it is also affected by the current in the armature. For our present purpose we treat it as constant.

There is yet another source of error which it is necessary to examine. Some part of the induction in the armature may pass through the shaft instead of through the iron plates. An idea of the amount of this disturbance may be readily obtained. Consider the closed curve ABCDEF, AB and FEDC are drawn along lines of force, AF and BC are orthogonal to lines of force. Since this closed curve has no currents passing through it, the line integral of force around it is nil; therefore, neglecting force along ED, we have force along AB is equal to force along FE and DC. In the machine presently described we may safely neglect the induction through the shaft; the error is comparable with the uncertainty as to the value of l_1; but in another machine, with magnets of much greater section, the effect of the shaft would become very sensible when the core is practically saturated.

The amended formula now becomes

$$4\pi nc = l_1 f\left(\frac{I}{A_1}\right) + 2l_2\frac{I}{A_2} + l_3 f\left(\frac{\nu I}{A_3}\right) + l_4 f\left(\frac{\nu I}{A_4}\right) + 2l_5 f\left(\frac{I}{A_5}\right)$$

where l_4 is the mean length of lines of force in the wrought-iron yoke, A_4 the area of the yoke, l_5 and A_5 corresponding quantities for the pole pieces, the last two terms being introduced for the forces required to magnetise the yoke and the two pole-pieces.

Fig. 2.

We now repeat the graphical method of construction exactly as before, the actual observations of induction in armature and current being plotted on the same diagram, Sheet II. (Plate 17), in which curve G represents the force required to magnetise the yoke, and curve H that required to magnetise the pole pieces. Before discussing these curves further, and comparing the results with those of actual observation, it may be convenient to describe the machine upon which the experiments have been made, confining the description strictly to so much as is pertinent to our present inquiry.

Description of Machine.

The dynamo has a single magnetic circuit, consisting of two vertical limbs, extended at their lower extremities to form the pole pieces, and having their upper extremities connected by a yoke of rectangular section. Each limb, together with its pole-piece, is formed of a single forging of wrought iron. These forgings, as also that for the yoke, are built up of hammered scrap and afterwards carefully annealed, and have a magnetic permeability but little inferior to the best Swedish charcoal iron. The yoke is held to the limbs by two bolts, the surfaces of contact being truly planed. In section the limb is oblong, with the corners rounded in order to facilitate the winding of the magnetising coils. A zinc base, bolted to the bed-plate of the machine, supports the pole-pieces.

The magnetising coils are wound directly on the limbs, and consist of 11 layers on each limb of copper wire 2·413 mms. diameter (No. 13, B.W.G.), making 3260 convolutions in all, the total length being approximately 4570 metres. The pole-pieces are bored to receive the armature, leaving a gap above and below, subtending an angle of 51° at the centre of the fields. The opposing surfaces of the gap are 8 mms. deep.

The following table gives the leading dimensions of the machine:—

	cms.
Length of magnet limb	=45·7
Width of magnet limb	=22·1
Breadth of magnet limb	=44·45
Length of yoke	=61·6
Width of yoke	=48·3
Depth of yoke	=23·2
Distance between centres of limbs	=38·1
Bore of fields	=27·5
Depth of pole-piece	=25·4
Width of pole-piece measured parallel to the shaft	=48·3
Thickness of zinc base	=12·7
Width of gap	=12·7

The armature is built up of about 1000 iron plates, insulated one from another by sheets of paper, and held between two end plates, one of which is secured by a washer shrunk on to the shaft, and the other by a nut and lock-nut screwed on the shaft itself. The plates are cut from sheets of soft iron, having probably about the same magnetic permeability as the magnet cores. The shaft is of Bessemer steel, and is insulated before the plates are threaded on.

The following table gives the leading dimensions of the armature:—

	cms.
Diameter of core	=24·5
Diameter of internal hole	= 7·62
Length of core over the end plates	=50·8
Diameter of shaft	= 6·985

The core is wound longitudinally according to the Hefner von Alteneck principle with 40 convolutions, each consisting of 16 strands of wire 1·753 mm. diameter, the convolutions being placed in two layers of 20 each. The commutator is formed of 40 copper bars, insulated with mica, and the connections to the armature so made that the plane of commutation in the commutator is horizontal, when no current is passing through the armature.

Plate 18, fig. 3 shows a side elevation of the dynamo; fig. 4 a cross-section through the centres of the magnets; fig. 5 a section of the core of the armature, in a plane through the axis of the shaft.

The dynamo is intended for a normal output of 105 volts 320 ampères at a speed of 750 revolutions per minute. The resistance of the armature measured between opposite bars of the commutator is 0·009947 ohm, and of the magnet coils 16·93 ohms, both at a temperature of 13·5° Centigrade; Lord RAYLEIGH's determination of the ohm being assumed.

We have now to estimate the lengths and areas required in the synthesis of the characteristic curve.

A_1;—from the length of the core of the armature (50·8 cms.) must be deducted 3·4 cms. for the thickness of insulating material between the plates; the resultant area is, on the other hand, as has already been stated, slightly augmented by the presence of the steel shaft. A_1 is taken as 810 sq. cms.

l_1;—this is assumed to be 13 cms.: *i.e.*, slightly in excess of the shortest distance (12·6 cms.) between the pole-pieces.

A_2;—the angle subtended by the bored face of the pole-piece at the axis is 129°, the breadth of the pole-piece is 48·3 cms., the diameter of the bore of the field is 27·5 cms., and, as already stated, the diameter of core 25·5 cms., thus, the area of pole-piece is 1513 sq. cms., and the area of 129° of the cylinder at the mean radius of 13·0 cms. is 1410 sq. cms; this value is taken for A_2 in the curves drawn on Sheet I. (Plate 16). In Sheet II. (Plate 17) A_2 is taken as 1600, an allowance of 190 sq. cms. being made for the spreading of the field at the edges of the pole-pieces, or $\frac{190}{160}=1·2$ cm. all round the periphery, that is $\frac{1·2}{1·5}=0·8$ of the distance from iron of pole-pieces to iron of core.

l_2 is 1·5 cm.

A_3 is a little uncertain as the forgings are not tooled all over, it is here taken as 930 sq. cms., but this value may be slightly too high.

l_3 is 91·4 cms.

A_4 is 1120 sq. cms.

l_4 is 49 cms., being measured along a quadrant from the centre of the magnet, thus:—

Fig. 3.

A_5 is 1230 sq. cms., intermediate between the area of magnet and face of pole-piece.

l_5 is 11 cms.

ν was determined by experiment as described below, and its value is taken as 1·32;

when the magnetising current is more than 5·62 ampères its value should be a little greater.

The function $f(a)$ is taken from HOPKINSON, Phil. Trans., vol. 176 (1885), p. 455; the wrought iron there referred to was not procured at the same time as, and its properties may differ to a certain extent from, the wrought iron of these magnets.

The curves now explain themselves, the abscissæ in each case represent the line integral of magnetising force in the part of the magnetic circuit referred to, the ordinates, the number of lines of induction which also pass through the armature.

The results of the actual observations on the machine are indicated, those when the magnetising force is increasing +, when it is decreasing ⊕. The measurements of the currents in the magnets which were separately excited, and of the potential difference between the brushes, the circuit being open, were made with Sir W. THOMSON'S graded galvanometers, standardised at the time of use. The irregularities of the observations are probably due to the variation of speed, the engine being not quite perfectly governed. The second construction exhibits quite as close an agreement between observation and calculation as could be expected; the deviation at high magnetising forces is probably due to three causes, increase in the value of ν when the core of the armature is partially saturated, uncertainty as to the area A_3, difference in the quality of the iron. It is interesting to see how clearly theory predicts the difference between the ascending and descending curves of a dynamo. Consideration of the diagram proves that this machine is nearly perfect in its magnetic proportions. The core might be diminished by increasing the hole through it to a small, but very small, extent without detriment. Any reduction of area of magnets would be injurious, they might, indeed, be slightly increased with advantage. An increase in the length of the magnets would be very distinctly detrimental. Again, little advantage results from increasing the magnetising force beyond the point at which the permeability of the iron of the magnets begins to rapidly diminish. For iron of the same quality as that of the machine under consideration, a magnetising force of $2·6 \times 10^3$ or 28·4 per centimetre is suitable. To get the same induction in other parts of the circuit, the diagram shows that for the air space a magnetising force of 21×10^3 is required, for the pole-pieces $0·1 \times 10^3$, for the armature $0·2 \times 10^3$, for the yoke $0·6 \times 10^3$, making a total force required of $24·5 \times 10^3$. Any alteration in the length or the area of any portion of the magnetic circuit entails a corresponding alteration in the magnetising forces required for that portion, at once deducible from the diagram. Similar machines must have the magnetising forces proportional to the linear dimensions, and, consequently, if the electromotive force of the machines is the same, the diameter of the wire of the magnet coils must be proportional to the linear dimensions. If the lengths of the several portions of the magnetic circuit remain the same, but the areas are similarly altered, the section of the wire must be altered in proportion to the alteration in the periphery of the section.

Experiment to determine ν.

Around the middle of one of the magnet limbs a single coil of wire was taken, forming one complete convolution, and its ends connected to a THOMSON's mirror galvanometer rendered fairly ballistic. If the circuit of the field magnets, while the exciting current is passing, be suddenly short-circuited, the elongation of the galvanometer is a measure of the total induction within the core of the limbs, neglecting the residual magnetisation. If the short circuit be suddenly removed, so that the current again passes round the field-magnets, the elongation of the galvanometer will be equal in magnitude and opposite in direction.

The readings taken were:

Zero	71	left.
Deflection	332	,, magnets made.
,, ...	196	right; magnets short-circuited.

Hence, deflection to right = 267

,, left = 261

Mean deflection = 264

To determine the induction through the armature, the leads to the ballistic galvanometer were soldered to consecutive bars of the commutator, connected to that convolution of the armature, which lay in the plane of commutation.

The readings taken were:

Zero	23	left.
Deflection	223	,, magnets made.
,, ...	176	right; magnets short-circuited.
,, ...	178	

Hence, deflection to right and left = 200

It thus appears that out of 264 lines of force passing through the cores of the magnet limbs at their centre, 200 go through the core of the armature, whence ν equals 1·32. The magnetising current round the fields during these experiments was 5·6 ampères.

Experiments on Waste Field not passing through Armature.

As in the determination of ν a single convolution was taken around the middle of one of the limbs, and connected to the ballistic galvanometer; the deflections, when a current of 5·6 ampères was suddenly passed through the fields or short-circuited, were:

Zero . . . . 34 left.
Deflection . . . . . 148 „ magnets made.
„ . . . . 82 right; magnets short-circuited.
Hence, deflection to right = 116
„ left = 114
Mean deflection = 115

I. Four convolutions were then wound round the zinc plate and the cast-iron bed in a vertical plane, passing through the axis of the armature; and the deflections noted:

Zero . . . . 15 left.
Deflection . . . . . 61 „ magnets short-circuited.
„ . . . . 40 right; magnets made.
Zero . . . . 11 left.
Deflection . . . . . 64 „ magnets short-circuited.
„ . . . . 36 right; magnets made.
Hence, deflection to right = 55
„ left = 46
and deflection to right = 47
„ left = 53

in the two observations respectively, giving a mean =50·25; or, reducing to one convolution, =12·6.

II. A square wooden frame, 38 cms. × 38 cms., on which were wound ten convolutions, was then inserted between the magnet limbs, with one side resting on the armature, and an adjacent side projecting 5 cms. beyond the coils on the limbs, or about 7·6 cms. beyond the cores of the limbs. The deflections were:

Zero . . . . 34 left.
Deflection . . . . . 98 „ magnets made.
„ . . . . 22 right; magnets short-circuited.
„ . . . . 21 „ „ „
„ . . . . 81 left; magnets made.
Hence, deflection to right = 56
„ left = 64
and „ right = 55
„ left = 47

in the two observations respectively, giving a mean =55; or, reducing to one convolution, =5·5.

III. The same frame was raised a height of 6·35 cms. above the armature in a vertical plane. The deflections were:

Zero	21 left.
Deflection	98 „ magnets made.
Zero	35 left.
Deflection	8 right; magnets short-circuited.

Hence, deflection to left $= 50$

„ right $= 43$

and mean deflection $= 46·5$

or, reducing to one convolution $= 4·6$.

IV. The same frame was again lowered on the armature and pushed inwards so as to lie symmetrically within the space between the limbs. The deflections were:

Zero	32 right.
Deflection	112 „ magnets made.
„	48 left; magnets short-circuited.

giving a mean of 80; or, reducing to one convolution, $=8·0$.

Let G represent the leakage through a vertical area bounded by the armature, and a line 7·6 cms. above the armature, and of the same width as the pole-pieces; let R be the remainder of the leakage between the limbs; then II. and III. give

$$\tfrac{2}{3}G+\tfrac{2}{3}R=5·5$$

$$\tfrac{2}{3}R=4·6$$

whence

$$G=1·35$$

$$R=6·9$$

Again IV. gives

$$\tfrac{5}{6}(G+R)=8·0$$

therefore

$$G+R=9·6$$

which shows an agreement as near as might be expected considering the rough nature of the experiment, and that the leakage is assumed uniform over the areas considered.

We take

$$G=1·6$$

$$R=8·0$$

Reducing these losses to percentages we have

$G=\frac{1\cdot 6}{115}$	$= 1\cdot 4$	per cent.
$R=\frac{8\cdot 0}{115}$	$= 7\cdot 0$	„
And from I. the leakage through the zinc plate and iron base	$=10\cdot 3$	„
Hence the two gaps account for	2·8	„
The zinc plate and iron base account for	10·3	„
And the area between the limbs	7·0	„
Making a total loss accounted for	20·1	„
Out of an observed loss of	24·24	„

The leakage through the shaft and from pole-piece to yoke, and one pole-piece to the other by exterior lines, will account for the remainder.

Effect of the Current in the Armature.

The currents in the fixed coils around the magnets are not the only magnetising forces applied in a dynamo machine; the currents in the moving coils of the armature have also their effect on the resultant field. There are in general two independent variables in a dynamo machine, the current around the magnets and the current in the armature, and the relation of E.M.F. to currents is fully represented by a surface. In well-constructed machines the effect of the latter is reduced to a minimum, but it can be by no means neglected. When a section of the armature coils is commutated it must inevitably be momentarily short-circuited, and if at the time of commutation the field in which the section is moving is other than feeble, a considerable current will arise in that section, accompanied by waste of power and destructive sparking. It may be well at once to give an idea of the possible magnitude of such effects. In the machine already described the mean E.M.F. in a section of the armature at a certain speed may be taken as 6 volts, its resistance 0·000995 ohm. Setting aside, then, for the moment questions of self-induction, if a section were commutated at a time when it was in a field of one-tenth part of the mean intensity of the whole field there would arise in that section, whilst short-circuited by the collecting brush, a current of 600 ampères, four times the current when the section is doing its normal work. The ideal adjustment of the collecting brushes is such that during the time they short-circuit the sections of the armature the magnetic forces shall just suffice to stop the current in the section, and to reverse it to the same current in the opposite direction.

Suppose the commutation occurs at an angle λ in advance of the symmetrical position between the fields, and that the total current through the armature be C, reckoned positive in the direction of the resultant E.M.F. of the machine, *i.e.*, positive when the machine is used as a generator of electricity. Taking any closed line through magnets and armature, symmetrically drawn as ABCDEFA (fig. 4), it is obvious that the line integral of magnetic force is diminished by the current in the armature included between angle λ in front and angle λ behind the plane of symmetry. If m be the number of convolutions of the armature, the value of this magnetising force is $4\pi C\frac{m}{2}\frac{2\lambda}{\pi}=4\lambda mC$ opposed to the magnetising force of the fixed coils on the magnets. Thus, if we know the lead of the brushes and the current in the armature we are at once in a position to calculate the effect on the electromotive force of the machine. A further effect of the current in the armature is a material disturbance in the distribution of the induction over the bored face of the pole-piece; the force along BC (fig. 4) is by no means equal to that along DE. Draw the closed curve BCGHB, the line integral along CG and HB is negligible. Hence the difference between force HG and BC is equal to $4\pi C\frac{m}{2}\frac{\kappa}{\pi}=2\kappa mC$ where κ is the angle COG.

Fig. 4.

This disturbance has no material effect upon the performance of the machine. But the current in the armature also distorts the arrangement of the comparatively weak field in the gap between the pole-pieces, displacing the point of zero field in the direction of rotation in a generator and opposite to the direction of rotation in a motor; and it is due to this that the non-sparking point for the brushes is displaced. A satisfactory mathematical analysis of the displacement of the field in the gap between the pole-pieces by the current in the armature would be more troublesome than an *à priori* analysis of the distribution of field in this space when the magnet current is the only magnetising force. Owing to the fact that the armature is divided into a finite number of sections there is a rapid diminution of the displacement of the field during the time that a section is being commutated, the diminution being recovered whilst the brush is in contact with only one bar of the commutator. The field thus oscillates slightly, owing to the disturbance caused by reversing the direction of the current in the successive sections of the armature. The number of oscillations in a GRAMME armature or in a SIEMENS' armature with an even number of sections will be ρm, where ρ is the number of revolutions per second, but in a SIEMENS' armature with an odd number of sections it will be $2\rho m$.* This oscillation of the field is only another way of expressing the effect of the self-induction of the section, but it must be remembered that if the self-induction, multiplied by change of current, is expressed as a change in the field we must omit self-induction as a separate term in our electrical equations. The precise lead to be given to the brushes in order to avoid sparking in any given case depends on many circumstances—the form and extent of the pole-pieces, the number of sections in the armature, and the duration of the short circuit which the brushes cause in any section of the armature. The adjustment of the position of the collecting brushes is generally made by hand at the discretion of the attendant, and is in some cases fixed once for all to suit an average condition of the machine. We shall, therefore, treat λ the lead as an independent variable, controlled by the attendant.

Let I be total induction through the armature, I+I′ total induction through the magnets, I′ being the waste field. Let C be current in armature, c in the magnets. Let gI′ be the line integral of magnetic force from a point on one pole-piece to a point on the other, the line being drawn external to the armature, g will be approximately constant. Omitting as comparatively unimportant the magnetising force in the pole-pieces and iron core of the armature we have the following equations:—

$$4\lambda mC+2l_2\frac{I}{A_2}-gI'=0$$

$$4\lambda mC+2l_2\frac{I}{A_2}+l_2f\left(\frac{I+I'}{A_2}\right)=4\pi nc.$$

When C=O we observed

$$I=\frac{1}{\nu-1}I'$$

whence

$$g=\frac{1}{\nu-1}\frac{2l_2}{A_2}$$

[* Added Aug. 17.—Armatures with an odd number of convolutions are open to one theoretical objection, which would be a practical one if the number of convolutions were very small. The $2m+1$ convolutions constitute in themselves a closed circuit, having a resistance four times the mean actual resistance of the armature measured between the collecting brushes. When any one convolution is exactly in the middle of the field the E.M.F. of the other $2m$ convolutions exactly balance, so that there is upon the closed circuit an E.M.F. due to the single convolution somewhat in excess of $\frac{1}{m}$th part of the actual E.M.F. of the machine. Thus there will be an alternating E.M.F. around the closed circuit of the armature capable of causing a considerable waste of power. This waste is materially checked by the self-induction of the circuit.]

eliminating I′

$$\frac{2l_2}{\nu A_2}\left(\nu I+4\lambda mC\frac{A_2}{2l_2}\nu-1)\right)+l_3 f\left\{\frac{\nu I+4\lambda mC\cdot\frac{A_2}{2l_2}(\nu-1)}{A_2}\right\}=4\pi nc+4\lambda mC\frac{\nu-1}{\nu}-4\lambda mC$$

$$=4\pi nc-4\lambda mC\frac{1}{\nu}.$$

The characteristic curve when $C=O$ being $I=F(4\pi nc)$ we may write the above as the equation of the characteristic surface thus

$$I+\frac{\nu-1}{\nu}4\lambda mC\frac{A_2}{2l_2}=F\left(4\pi nc-\frac{4\lambda mC}{\nu}\right).$$

In applying this equation it must not be forgotten that the E.M.F. of the machine cannot be determined from I unless the commutation occurs at such a time that the coil being commutated embraces all, or nearly all, the lines of induction in the armature.

This equation enables the characteristic surface to be constructed from the characteristic curve. Let $OL=4\pi nc$, $LM=4m\lambda C$, draw MK so that $\frac{KL}{LM}=\frac{1}{\nu}$, through K draw ordinate KR meeting characteristic curve in R, draw RQ parallel to OL meeting ordinate QL in Q, draw QS parallel to LM; draw QP so that $\frac{PS}{SQ}=\frac{\nu-1}{\nu}\cdot\frac{A_2}{2l_2}$. Then P is a point on the characteristic surface.

Fig. 5.

A very important problem is to deduce the characteristic curve of a series wound machine from the normal characteristic; in this case $c=C$, and we have

$$I+\frac{\nu-1}{\nu}4\lambda mC\frac{A_2}{2l_2}=F\left\{\left(4\pi n-\frac{4\lambda m}{\nu}\right)C\right\}$$

taking PR as ordinate of any point in the normal characteristic, cut off QR equal to $\frac{\nu-1}{\nu}4\lambda m\mathrm{C}\frac{\mathrm{A}_2}{2l_2}$, that is, draw OQ so that

$$\tan \mathrm{QO}x=\frac{\nu-1}{\nu}4\lambda m\mathrm{C}\frac{\mathrm{A}_2}{2l_2}\Big/4\pi\left(n-\frac{m\lambda}{\nu\pi}\right)\mathrm{C}$$

$$=\frac{\nu-1}{\nu}\frac{\mathrm{A}_2}{2l_2}\frac{\lambda m}{\pi n-\frac{\lambda m}{\nu}}$$

then PQ will represent the induction corresponding to magnetising force $4\pi\left(n-\frac{m\lambda}{\nu\pi}\right)\mathrm{C}$.

Fig. 6.

It is noteworthy that as the current C, and therefore OR increases, PQ, the induction, will attain a maximum and afterwards diminish, vanish, and become negative. That in series wound machines the E.M.F. has a maximum value has been many times observed. The cause lies in the existence of a waste field not passing through the armature, and in the saturation of the magnet core.

The effect of the current in the armature on the potential between the brushes of any machine is the same as that of an addition to the resistance of the armature proportional to the lead of the brushes, and to the ratio of the waste field to the total field, combined with that of taking the main current $\frac{m\lambda}{\nu\pi}$ times round the magnets in direction opposite to the current c. The preceding investigation tells the whole story of a dynamo machine, excepting only the relation of λ to C in order that the brushes may be so placed as to avoid sparking. The only constant or function which has to be determined experimentally for any particular machine is ν, the ratio of total to effective field, all the rest follows from the configuration of the iron and the known properties of the material.

The following illustrations of the effect of the current in the armature and the lead of the brushes are interesting. In both cases the magnet coils are supposed to be entirely disconnected so that c is zero. First, let λ be negative, short circuit the brushes and drive the machine at a certain speed, a large current will be produced, the current in the armature itself forming the magnet.* Second, let λ be positive, cause a current to pass through the armature, the armature will turn in the positive direction and will act as a motor capable of doing work. In either case, particularly the former, such use of the machine would not be practical owing to violent sparking on the commutator. The following is a further illustration of the formula given above. If we could put up with the sparking which would ensue, it would be possible to make λ negative in a generator of electricity, and thereby obtain by the reactions of the armature itself all the results usually obtained by compound winding.

Efficiency Experiments.

Having discussed the relations subsisting between the configuration of the magnetic circuit of a dynamo machine and the induction obtained for given magnetising forces, and having compared the results obtained by direct calculation with the results of actual observation on a particular machine, the construction of which we have described at length, it appeared of importance to determine the efficiency of the machine under consideration as a converter of energy, when used either as a generator of electricity or as a motor. An accurate determination of the mechanical power transmitted to a dynamo by a driving belt, or of the power given by a motor presents formidable experimental difficulties. Moreover, if the mechanical power absorbed in driving the dynamo be measured directly, any error in measurement will involve an error of the same magnitude in the determination of the efficiency. To avoid this difficulty, we employed the following device.

Let two dynamos, approximately equal in dimensions and power, have their shafts coupled by a suitable coupling, which may serve also as a driving pulley; and let the electrical connexions between the dynamos be made so that the one drives the other as a motor. If the combination be driven by a belt passing over the coupling pulley, the power transmitted by the belt is the waste in the two dynamos and the connexions

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[* Added Aug. 17.—This experiment was tried upon a dynamo machine of construction generally similar to that shown in figs. 3, 4, 5, Plate 18, but with an armature of half the length intended in normal work to give 400 ampères 50 volts at 1000 revolutions. The magnet coils were disconnected, and the terminals of the armature were connected through a SIEMENS's electro-dynamometer, and the machine was run at 1380 revolutions. When the brushes were placed in the normal position ($\lambda=0$) the current due to residual magnetism was 52 ampères. By giving the brushes a small positive lead the current was reduced to nearly zero. By giving the brushes a small negative lead a current of over 234 ampères, the maximum measured by the dynamometer, was obtained, and by varying the lead it was easy to maintain a steady current of any desired amount.]

between them. By suitably varying the magnetic field of one of the dynamos, the power passing between the two machines can be adjusted as desired. If, then, the electrical power given out by the generator is measured, and also the power transmitted by the belt, the efficiency of the combination can be at once determined. By this arrangement the measurement, which presents experimental difficulties, viz., the power transmitted by the belt, is of a small quantity. Consequently, even a considerable error in the determination has but a small effect on the ultimate result. On the other hand, the measurement of the large quantity involved, viz., the electrical power passing between the two machines, can without difficulty be made with great accuracy.

The second machine was similar in all respects to that already described, and each is intended for a normal output of 110 volts, 320 ampères, at a speed of 780 revolutions per minute.

The power transmitted by the belt was measured by a dynamometer of the HEFNER-ALTENECK type, the general arrangement being as shown in the diagram, Plate 18. A is the driving pulley of the engine, B the driven coupling of the dynamos; D, D are the guide pulleys of the dynamometer carried on a double frame turning about the fulcrum C, and supported by a spiral spring, the suspension of which can be varied by a pair of differential pulley-blocks attached to a fixed support overhead. When a reading is made the suspension of the spring is adjusted until the index of the dynamometer comes to a fiducial mark on a fixed scale, the extension of the spring is then read by a second index attached to its upper extremity; F, F are two fixed guide pulleys of the same diameter as the pulleys D, D, and having the same distance between their centres, in order that the two portions of the belt may be parallel and the sag as far as possible taken up. The normal from C to the centre line of either portion of the belt between the pulley A and the guide pulleys = 31·9 cms. The normal from C to the centre line of either of the parallel portions of the belt = 2·4 cms.; and from C to the centre line of the spring = 92·7 cms.

Take moments about C; then

$$\text{Tension of the belt} = \frac{92{\cdot}7}{34{\cdot}3} \times \text{tension of spring},$$
$$= 2{\cdot}7 \times \text{tension of spring}.$$

Also the diameter of the pulley B = 33·6 cms. and the thickness of the belt = 1·6 cm.

Hence the velocity of the centre of the belt in centimetres per second = 1·845 × revolutions of dynamo per minute, and, therefore,

Power transmitted by the belt in ergs per second

$$= 2{\cdot}7 \times 1{\cdot}845 \times 981 \times \text{tension of spring} \times \text{revolutions per minute},$$

assuming the value of g to be 981.

We may more conveniently express the power in watts ($=10^7$ ergs per second), and write

Power in watts = ·0004887 × tension of spring × revolutions per minute.

The potential between the terminals of the generator was measured by one of Sir William Thomson's graded galvanometers, previously standardised by a Clark's cell, which had been compared with other Clark's cells, of which the electromotive force was known by comparison with Lord Rayleigh's standard. The current between the two machines was measured by passing it through a known resistance, the difference of potential between the ends of the resistance being determined by direct comparison with the Clark's standard cell, according to Poggendorff's method. As experiments were made with currents of large magnitude, it was important that the temperature coefficient of the resistance should be as low as possible. To this end we found a resistance-frame constructed of platinoid wire of great value. The temperature coefficient of this alloy is only 0·021 per cent. per degree Centigrade. (Proc. Roy. Soc., vol. 38, p. 265 (1885.)

The resistances of the armatures and magnets of the two machines are as follows:—

		Ohms.
Generator . . .	armature . . .	0·009947
	magnets. . . .	16·93
Motor.	armature . . .	0·009947
	magnets. . . .	16·44

The resistance of the leads connecting the two machines was 0·00205 ohm, and of the standard resistance 0·00586 ohm.

In all determinations of resistance, the value of the B.A. ohm was taken as $0·9867 \times 10^9$ c.g.s. units, according to Lord Rayleigh's determination.

The diagram shows the electrical connexions between the two machines with the rheostat r inserted in the magnets of the motor dynamo.

In order to ascertain the friction of bending the belt round the pulley B, and of the journals of the dynamo, a preliminary experiment was made with the dynamometer. The combination was run at a speed of 814 revolutions per minute with the dynamos on open circuit and the tension of the spring observed—9979 grammes. The engine was then reversed, and the dynamos run at the same speed and the tension of the spring again observed—3629 grammes. The difference of the two readings gives twice the power absorbed in friction, viz.: 1262 watts for the two machines, or 631 watts per machine. This is excluded entirely from the subsequent determinations of efficiency, as being a quantity dependent on such arbitrary conditions as the lubrication of the journals, the weight of the belt, and the angle it makes with the horizontal.

TABLE I.

	I. Revolutions per minute.	II. Grammes.	III. Watts.	IV. Volts.	V. Ampères.	VI. Ohms.	VII. Watts.	VIII. Watts.	IX. Watts.	X. Watts.	XI. Watts.	XII. Watts.	XIII. Watts.	XIV. Watts.
1	810	8,392	3324	129·1	21·6	1·39	13	4	984	861	110	4,720	676	5,396
2	801	9,299	3642	127·2	72·0	1·39	75	62	955	770	130	10,678	825	11,503
3	811	11,113	4413	125·8	150·0	2·72	267	223	935	825	294	21,014	935	21,949
4	808	10,433	4116	124·4	186·0	2·72	394	344	914	695	387	25,256	691	25,947
5	792	10,660	4124	116·5	211·0	2·72	501	445	801	608	454	26,592	657	27,249
6	798	16,897	6595	110·6	351·0	4·59	1317	1231	722	581	1099	41,567	822	42,389
7	764	17,690	6604	110·12	358·0	4·09	1360	1274	716	472	1117	42,086	831	42,917
8	766	17,804	6669	110·6	360·0	4·59	1335	1296	722	452	1151	42,451	856	43,307
9	778	16,556	6300	102·3	369·0	4·09	1443	1361	618	396	1176	40,304	653	40,957
10	756	20,412	7537	96·8	446·0	4·59	2070	1978	554	348	1668	46,242	459	46,701
11	808	9,526	4758	119·3	36·8	2·72	394	344	855	636	211	7,011	1009	8,020
12	802	..	1512	113·5	No current	..	..	..	..	..	..	..	756	..
13	814	3,175	1262	..	..	..	..	..	..	..	..	..	631	..

In Table I. column I. is the speed of the dynamos; column II. is the reading of the spring in grammes; column III. is the power transmitted by the belt in watts; column IV. is the potential at the terminals of the generator; column V. is the current passing in the external circuit between the two machines; column VI. is the resistance introduced into the magnets of the motor by the rheostat; column VII. is the power absorbed in the armature of the generator; column VIII. is the power absorbed in the armature of the motor; column IX. is the power absorbed in the magnets of the generator; column X. is the power absorbed in the magnets of the motor; column XI. is the power absorbed in the connecting leads between the two dynamos, in the rheostat resistance *r*, and in the standard resistance used for measuring the current; column XII. is the total electrical power developed in the generator; column XIII. is half the power absorbed by the combination less the known losses in the armatures, magnets, and external connexions of the two machines; column XIV. is the total mechanical power given to the generator, being the sum of the powers given in columns XII. and XIII.

TABLE II.

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.
1	0·25	18·23	12·52	69·0	71·44	40·44
2	0·65	8·30	7·17	83·88	69·9	58·63
3	1·235	4·27	4·27	90·22	89·68	79·9
4	1·52	3·53	2·66	92·29	92·78	85·63
5	1·84	2·94	2·415	92·81	93·70	86·51
6	3·11	1·70	1·94	93·25	93·79	87·45
7	3·17	1·66	1·94	93·23	93·37	87·05
8	3·08	1·67	1·98	93·27	93·99	87·26
9	3·525	1·51	1·59	93·37	94·02	87·49
10	4·47	1·20	1·00	93·39	93·62	87·43
11	0·31	3·53	2·66	92·29	92·78	85·63

In Table II. the percentage losses in the armature and magnets of the generator are given, as also the sum of all other losses as obtained from column XIII. in the foregoing table; also the percentage efficiency of the generator, of the motor, and of the double conversion. Column I. is the percentage loss in the generator armature; column II. is the percentage loss in the generator magnets; column III. is the percentage sum of all other losses in the generator; column IV. is the percentage efficiency of the generator; column V. is the percentage efficiency of the motor; column VI. is the percentage efficiency of the double conversion.

In this series of experiments in all cases, from Nos. 1 to 10 inclusive, the brushes, both of the generator and motor, were set at the non-sparking point; but in No. 11 no lead was given to the brushes of the generator, and, consequently, there was violent sparking throughout the duration of the experiment.

In No. 12 the magnets were separately excited with a current giving 113·5 volts across their terminals. The power absorbed must be due entirely to local currents in the core of the armature, and the energy for the reversal of magnetisation of the core twice in every revolution of the armature.

No. 13 gives the results of the experiments on the friction of the bearings and in bending the belt already referred to.

It will be observed that the figures in column XIII. are calculated by deducting the power absorbed in the armatures and magnets, and extraneous resistances from the total power given to the combination as measured by the dynamometer. They must therefore include all the energy dissipated in the core of the armature, whether in local currents or in the reversal of its magnetisation; also the energy dissipated in local currents in the pole-pieces, if such exist; also the energy spent in reversing the direction of the current in each convolution of the armature as they are successively short circuited by the brushes. Further, it will include the waste in all the connexions of the machine from the commutator to its terminals and the friction of the brushes against the commutator. A separate experiment was made to determine the amount of this last constituent, but it was found to be too small to be capable of direct measurement by the dynamometer. Moreover, from the manner in which the figures in this column are deduced, any error in the dynamometric measurement will appear wholly in them. Since, undoubtedly, the first two components enumerated are the most important, and the conditions determining their amount are practically the same throughout the series, the close agreement of the figures in the column are a fair criterion of the accuracy of the observations. Probably 100 watts is the limit of error in any of the measurements. Such an error would affect the determination of the efficiency when the machines were working up to their full power to less than $\frac{1}{2}$ per cent.

It has been assumed that the sum of these losses is equally divided between the two machines. This will not accurately represent the facts, as the intensities of the fields and the currents passing through the armatures differ to some extent in the two machines. The inequality, however, cannot amount to a great quantity, and if it diminishes the efficiency of the generator it will increase the efficiency of the motor by a like amount, and contrariwise. In No. 11 of the series the effect of the sparking at the brushes of the generator is very marked, the power wasted amounting to at least 250 watts.

If it be assumed that the dissipation of energy is the same whether the magnetisation of the core is reversed by diminishing and increasing the intensity of magnetisation without altering its direction, or whether it is reversed by turning round its direction without reducing its amount to zero, a direct approximation may be made to the value of this component. (J. HOPKINSON, Phil. Trans., vol. 176 (1885), p. 455.)

The core has about 16,400 cubic centims. of soft iron plates, hence loss in magnetising and demagnetising when the speed is 800 revolutions per minute $=16,400 \times \frac{800}{60} \times 13,356$ ergs per second $=292$ watts.

Referring to Table II. it appears that the efficiency approaches a maximum when the current, passing externally between the two machines, is about 400 ampères. Let C be the current in the armature, ρ its resistance, W the power absorbed in all parts of the machine other than the armature, then, if the speed is constant, the efficiency is approximately $\frac{EC-W-C^2\rho}{EC}$, where E is the electromotive force. This is a maximum when $\frac{W}{C}+C\rho$ is a minimum, which occurs when $W=C^2\rho$; when the loss in the armature is equal to the sum of all other losses. For the machines under consideration the experimental results verify this deduction. But in actual practice the rate of generation of heat in the armature conductors, when a current of 400 ampères was passed for a long period, would be so great as to trench upon the margin of safety desirable in such machines. Of the total space, however, available for the disposition of the conductors only about one-fourth part is actually occupied by copper, the remainder being taken up with insulation, and the interstices left by the round wire. If the space occupied by the copper could be increased to three-fourths of the total space available, while the cooling surface remained the same, the current could be increased 75 per cent. and the efficiency increased 1·3 per cent. approximately, as all losses other than that in the armature-wires would not be materially altered.

The loss in the magnets is also susceptible of reduction. It has already been shown that for a given configuration of the magnetic circuit and a given electromotive force the section of the wire of the magnet coils is determinate. The length is, however, arbitrary, since within limits the number of ampère convolutions is independent of the length. An increase in the length will cause a proportionate diminution in the power absorbed in the magnet coils. If the surface of the magnets is sufficient to dissipate all the heat generated, then the length of wire is properly determined by Sir WILLIAM THOMSON's rule that the cost of the energy absorbed must be equal to the continuing cost of the conductor.

APPENDIX.

(Added Aug. 17.)

Since the reading of the present communication experiments have been tried on machines having armatures wound on the plan of GRAMME and with differently arranged magnets, the experiments were carried out in a closely similar manner to that already described.

Description of Machines.

The construction of these machines is shown in Plate 20, in which fig. 1 shows an elevation, fig. 2 a section through the magnets, fig. 3 a longitudinal section of the

25.

armature. It will be observed that the magnetic circuit is divided. The pole-pieces are of cast iron and are placed above and below the armature, and are extended laterally. The magnet cores are of wrought iron of circular section and fit into the extensions of the cast iron pole-pieces, so that the area of contact of the cast iron is greater than the area of section of the magnet. The magnetising coils consist of 2196 convolutions on each limb of copper wire, No. 17, B.W.G., in No. 1 machine, and 2232 convolutions in No. 2 machine. The pole-pieces are bored to receive the armature leaving a gap on either side subtending an angle of 41° at the axis.

The bearings are carried upon an extension of the lower pole-piece.

The following table gives the principal dimensions of the magnets in No. 1 machine :—

	cms.
Length of magnet limbs between pole-pieces . .	26·0
Diameter of magnet limb	8·6
Bore of fields	25·7
Width of pole-piece parallel to the shaft	24·1
Width of gap between poles	8·6

The armature is built up of plates as in the machine already described, and is carried from the shaft by a brass frame between the arms of which the wires pass.

The principal dimensions are as follows :—

	cms.
Diameter of core	24·1
Diameter of hole through core	14·0
Length of core over end plates	24·1

The core is wound on GRAMME's principle with 160 convolutions, each consisting of a single wire, No. 10, B.W.G., the wire lying on the outside of the armature in a single layer. The commutator has 40 bars.

This dynamo is compound wound, and is intended for a normal output of 105 volts 130 ampères, at a speed of 1050 revolutions per minute. The resistance of the armature is 0·047 ohm, and of the magnet shunt coils 53·7 ohms.

There is here no yoke, and consequently A_4 and l_4 do not appear in the equation.

It is necessary to bear in mind that the magnetising force is that due to the convolutions on one limb, and that the areas are the sums of the areas of the two limbs. In calculating induction from E.M.F. it is also necessary to remember that two convolutions in a GRAMME count as one in a HEFNER-ALTENECK armature.

A_1;—the section of the core is 245 sq. cms., allowances for insulation reduce this to 220·5 sq. cms.

l_1;—this is assumed to be 10 cms., but it will be seen that an error in this value has a much more marked effect on the characteristic in this machine than in the other.

A_2;—the angle subtended by the bored face of the pole-pieces is 139°, the mean of the radii of the pole-pieces and the core is 12·45 cms. Hence the area of 139° of the cylinder of this radius is 768·3 sq. cms., add to this a fringe of a width 0·8 of the distance from core to pole-pieces as already found necessary for the other machine, and we have 839·5 sq. cms. as the value of A_2.

l_2 is 0·8 cm.

A_3 is 365 sq. cms. (*i.e.*, the area of two magnet cores).

l_3 is 26·0 cms.

A_5 is taken to be 955 sq. cms., viz., double the smallest section of the pole-piece.

l_5 is a very uncertain quantity; it is assumed to be 15 cms.

The expression already used requires slight modification. Inasmuch as the pole-pieces are of cast iron a different function must be used. Different constants for waste field must be used for the field, the pole-pieces and the magnet core. We write

$$4\pi nc = l_1 f\left(\frac{I}{A_1}\right) + 2l_2\frac{\nu_2 I}{A_2} + l_3 f\left(\frac{\nu_3 I}{A_3}\right) + 2l_5 f'\left(\frac{\nu_5 I}{A_5}\right)$$

the function f' is taken from HOPKINSON, Phil. Trans., vol. 176 (1885), p. 455, Plate 52. ν_2, ν_3, and ν_5 were determined by experiment as described below, their values are

$$\nu_2 = 1{\cdot}05$$
$$\nu_3 = 1{\cdot}18$$
$$\nu_5 = 1{\cdot}49$$

Comparing the curves on Plate 17 with that on Plate 19, the most notable difference is that in the present case the armature core is more intensely magnetised than the magnet cores. No published experiments exist giving the magnetising force required to produce the induction here observed in the armature core, amounting to a maximum of 20,000 per sq. cm. We might, however, make use of such experiments as the present to construct roughly the curve of magnetisation of the material; thus we find that with this particular sample of iron a force of 740 per cm. is required to produce induction 20,000 per sq. cm.; this conclusion must be regarded as liable to considerable uncertainty.

The observations on the two machines are plotted together, but are distinguished from each other as indicated. They are unfortunately less accurate than those of Plate 17, and are given here merely as illustrating the method of synthesis.

Experiments to determine ν_2, ν_3, and ν_5.

The method was essentially the same as is described on pp. 338 and 339, and was only applied to No. 1 machine. Referring to fig. 7 a wire AA was taken four times round the middle of one limb of the magnet, a known current was suddenly passed round the magnets, the elongation of the reflecting galvanometer was observed, it was found to be 214 scale divisions, giving 107 as the induction through the two magnet limbs in terms of an arbitrary unit. The coil was moved to the top of the limb as at BB—the elongation was reduced to 206 or 103 for the two limbs. We take the mean induction in the magnet to be 105. A wire was taken three times round the whole armature in a horizontal plane as at CC; the elongation observed was 222 divisions or 74 in terms of the same units. A wire was taken four times round one-half of the armature as at DD; the elongation was 141, or induction in the iron of the armature 70·5, whence we have

$$\nu_2 = \frac{74}{70 \cdot 5} = 1 \cdot 05.$$

It may be well to recall here that ν_2 is essentially dependent on the intensity of the field, strictly the line B on Plate 19 should not be straight but slightly curved.

Four coils were taken round the upper pole-piece at EE; the elongation was 159, giving 79·5 on the two sides. Coils at FF give a higher result, 87·5, owing to the lines of induction which pass round by the bearings of the machine, and across to the upper ends of the magnets—ν_5 is taken to be $\frac{83 \cdot 5}{70 \cdot 5} = 1 \cdot 18$.

Fig. 7.

Efficiency Experiments.

The method and instruments were those already described, pp. 346 and 347, excepting that the current was measured by a THOMSON'S graded galvanometer, which had been standardised against a CLARK'S cell in the position and at the time when used. The resistance of leading wires and galvanometer was 0·034 ohm, the series coils introduced for compounding the machines were also brought into use, and the losses due to their resistance find a place in columns XII. and XIII. of the following Table III., in which column I. is lead of brushes of the dynamo, positive for the generator, negative for the motor; column II., revolutions per minute; column III., deflection of spring in grammes; column IV., watts by dynamometer; column V., volts at

TABLE III.

	I. Degrees.	II. Revolutions.	III. Grammes.	IV. Watts.	V. Volts.	VI. Ampères.	VII. Ohms.	VIII. Watts.	IX. Watts.	X. Watts.	XI. Watts.	XII. Watts.	XIII. Watts.	XIV. Watts.	XV. Watts.	XVI. Watts.	XVII. Watts.
1	17·5°	1098	7711	4419	100·1	139·0	∞ty	955	895	372	0	497	464	657	16,395	289	16,684
2	5°	1094	2722	1554	103·8	41·2	18·8	105	78	400	138	55	41	148	5,015	294	5,309
3*	0°	1144	1814	1083	104·7	7·85	0	11	3	395	409	6	1	2	1,637	128	1,765

* In this experiment the direction of the current had become reversed, and No. 2 machine was generator.

TABLE IV.

	Generator armature.	Generator shunt coils.	Generator series coils.	Other losses.	Efficiency of generator.	Efficiency of motor.	Efficiency of double conversion.
1	5·8	2·2	3·0	1·9	87·1	89·0	77·5
2	2·0	7·5	1·0	5·5	84·0	92·0	77·7

terminals of generator; column VI., ampères in external circuit; column VII., rheostat resistance; column VIII., watts in generator armature; column IX., watts in motor armature; column X., watts in generator shunt magnet coils; column XI., watts in motor shunt; column XII., watts in generator series magnet coils; column XIII., watts in motor series; column XIV., watts in external resistances; column XV., total electrical power of generator; column XVI., half the sum of losses unaccounted for; column XVII., total mechanical power applied to generator.

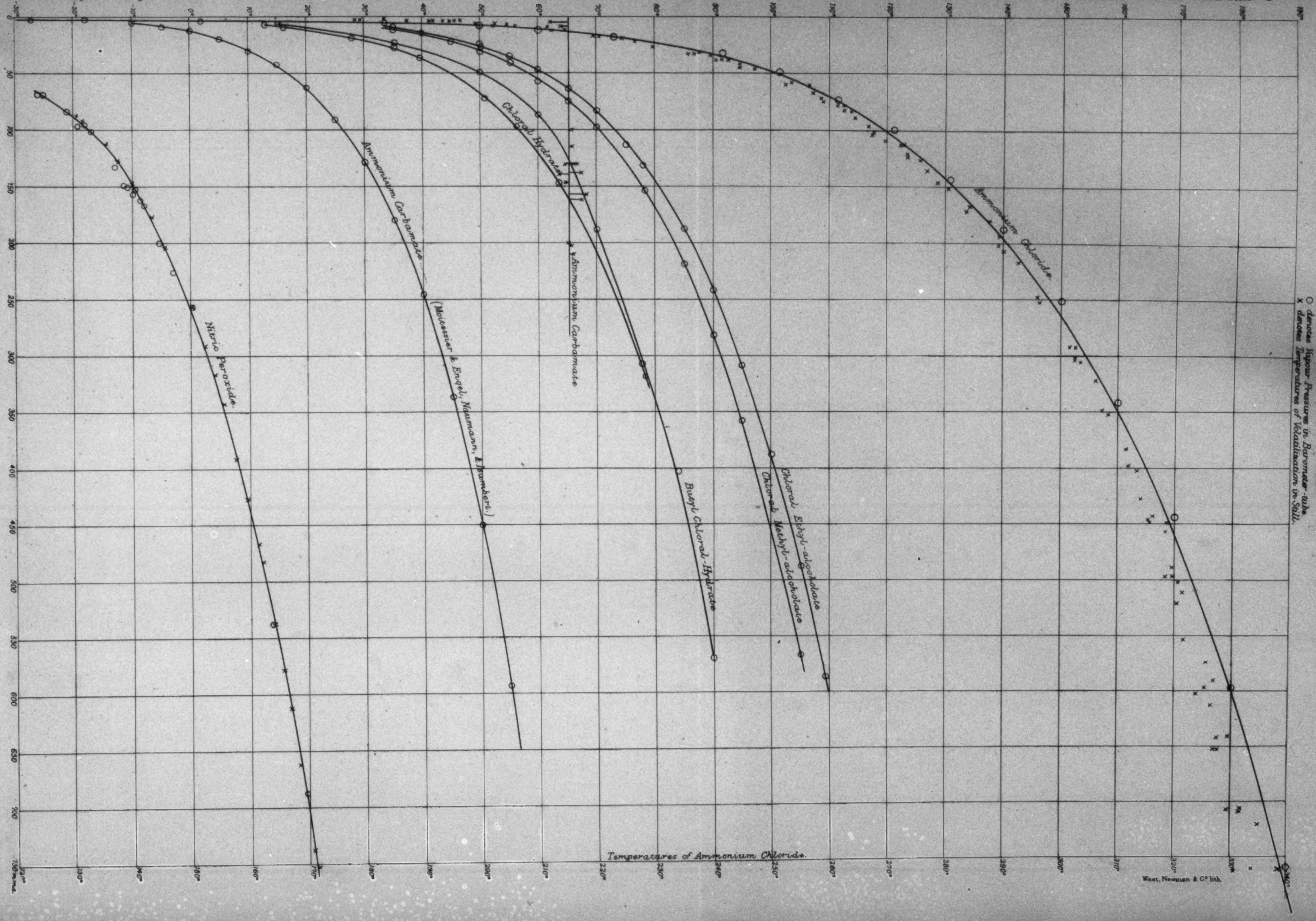
Table IV. gives the losses and efficiencies as percentages in exactly the same way as in Table II., excepting that another column is introduced for the loss in the series coils of the magnets of the generator.

The core of the armature contains about 6500 cub. cms. of iron. Hence energy of magnetising and demagnetising when the speed = 1100 revolutions per minute $=6500\times\frac{1100}{60}\times 13{,}356$ in ergs per second = 159 watts.]

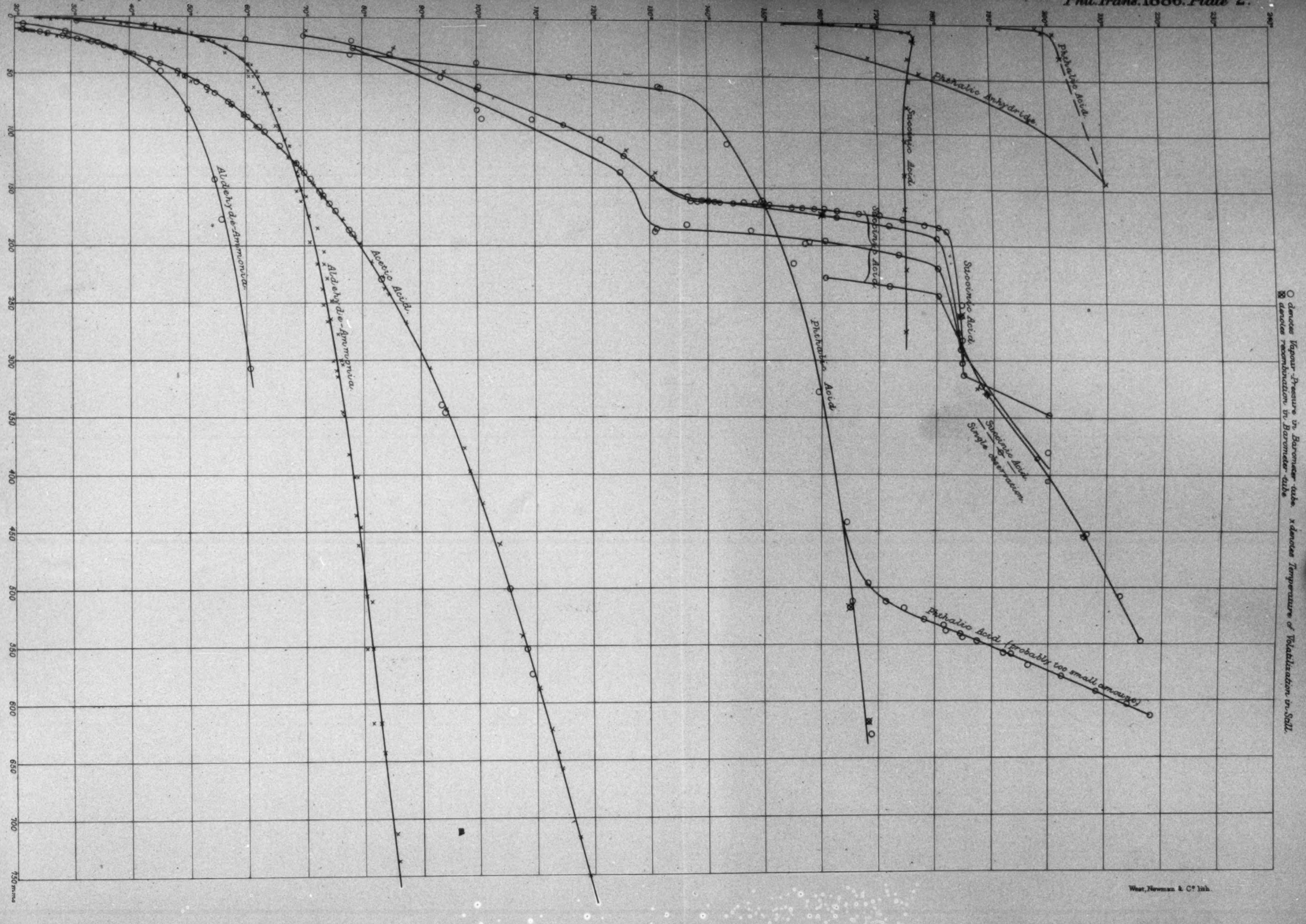
In conclusion we desire to express our indebtedness to Messrs. Mather and Platt, by whom the machines we have used were manufactured, and who, in placing the same at our disposal, together with all facilities for carrying out our experiments at their Salford Iron Works, have enabled us to put theory to the test of experiment on an engineering scale.

Ramsay & Young.

Phil. Trans. 1886. Plate 1.



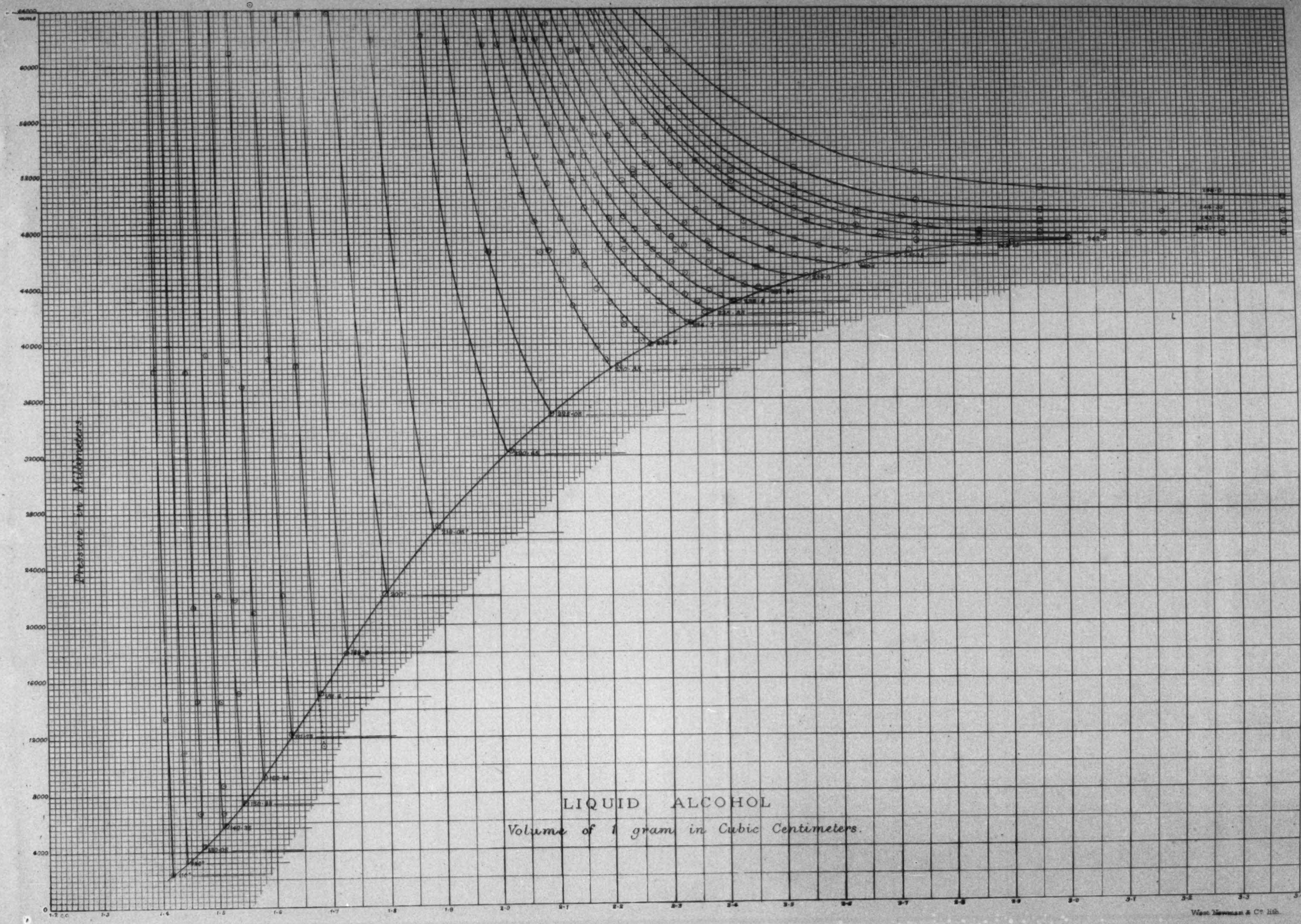
West, Newman & Co. lith.



West, Newman & Co lith.

Ramsay & Young.

Phil. Trans. 1886. Plate 3.



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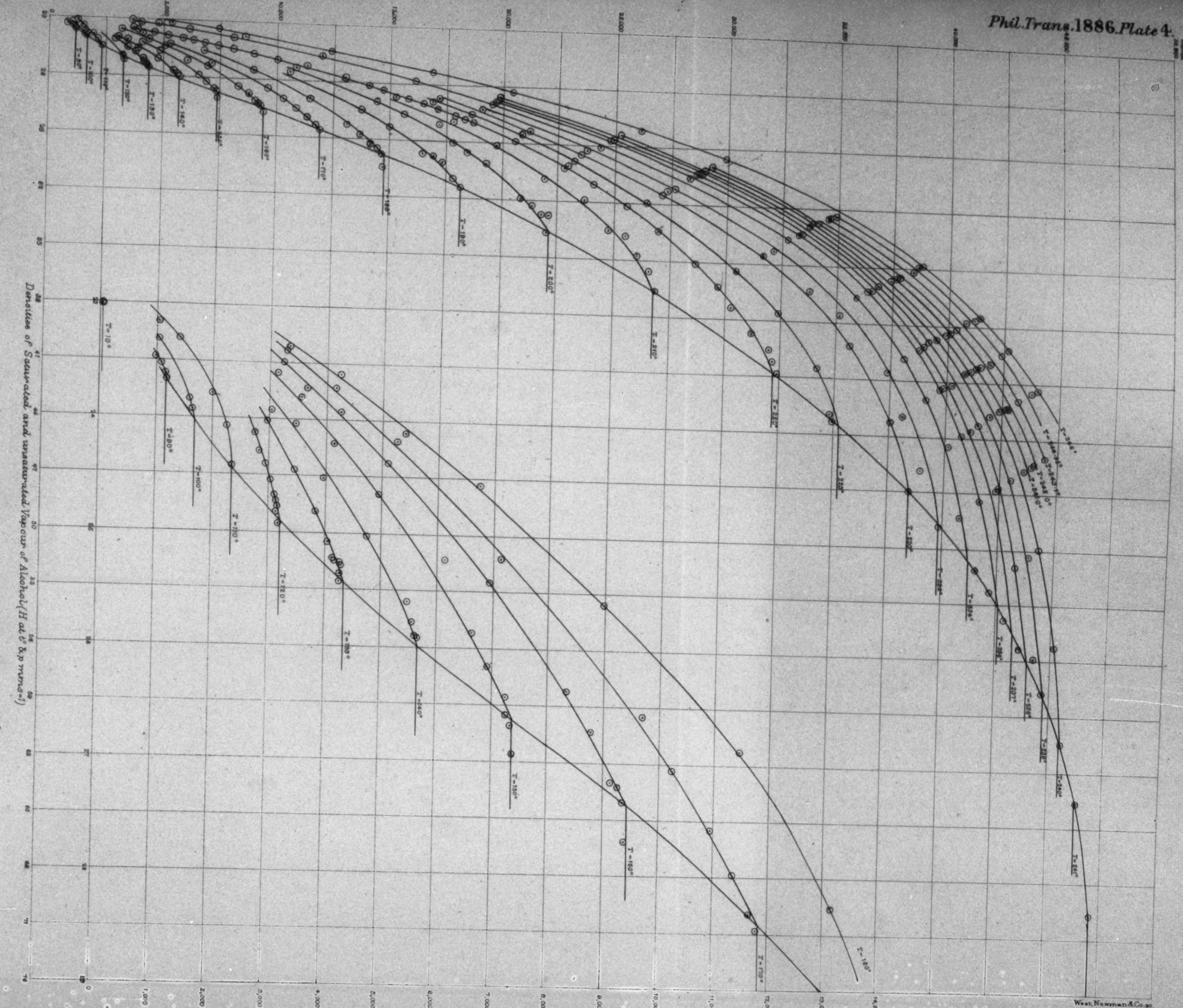


West, Newman & Co. sc.

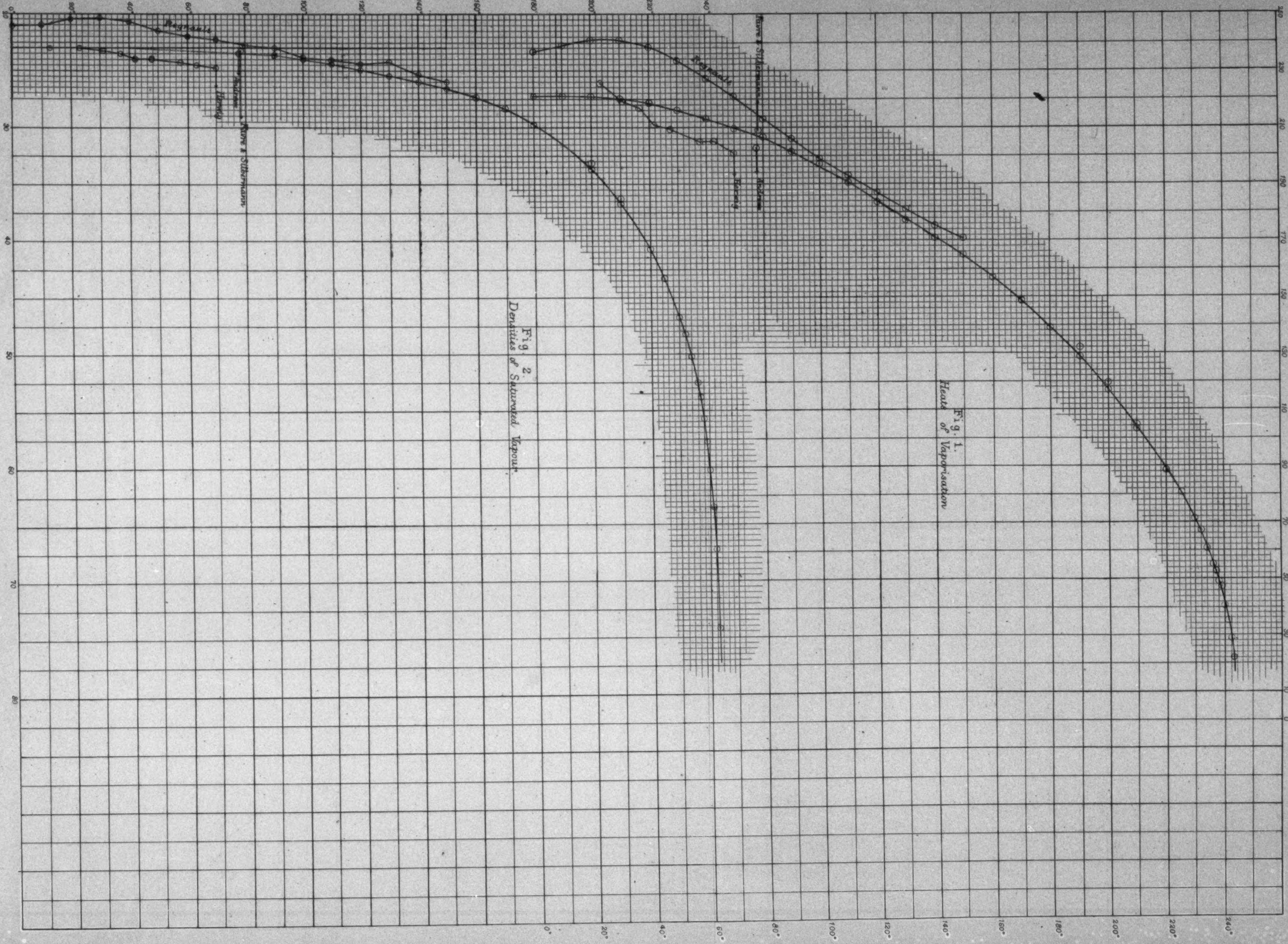
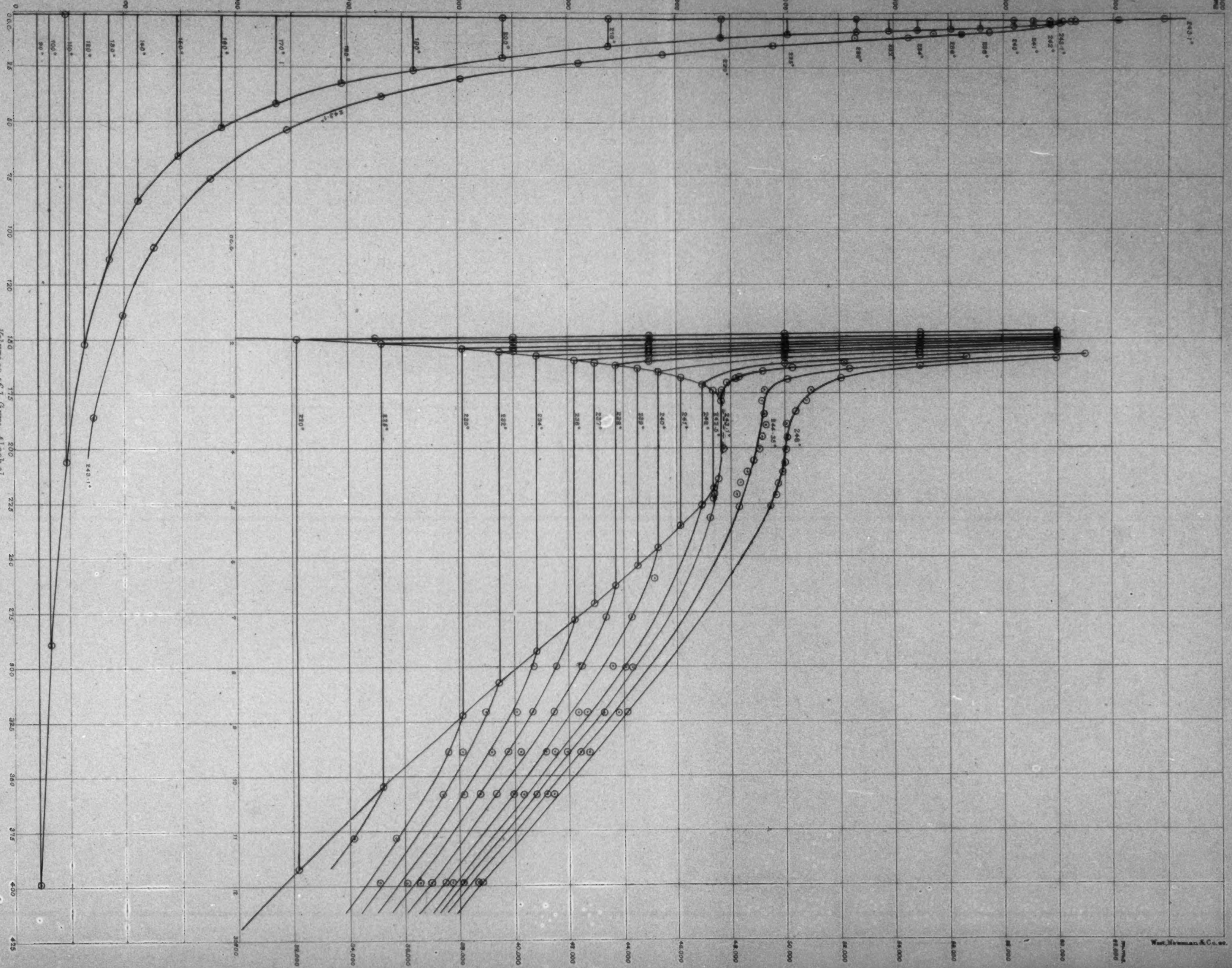


Fig. 2. Densities of Saturated Vapour.

Fig. 1. Heats of Vaporisation.

Ramsay & Young.

Phil. Trans. 1886. Plate 6.



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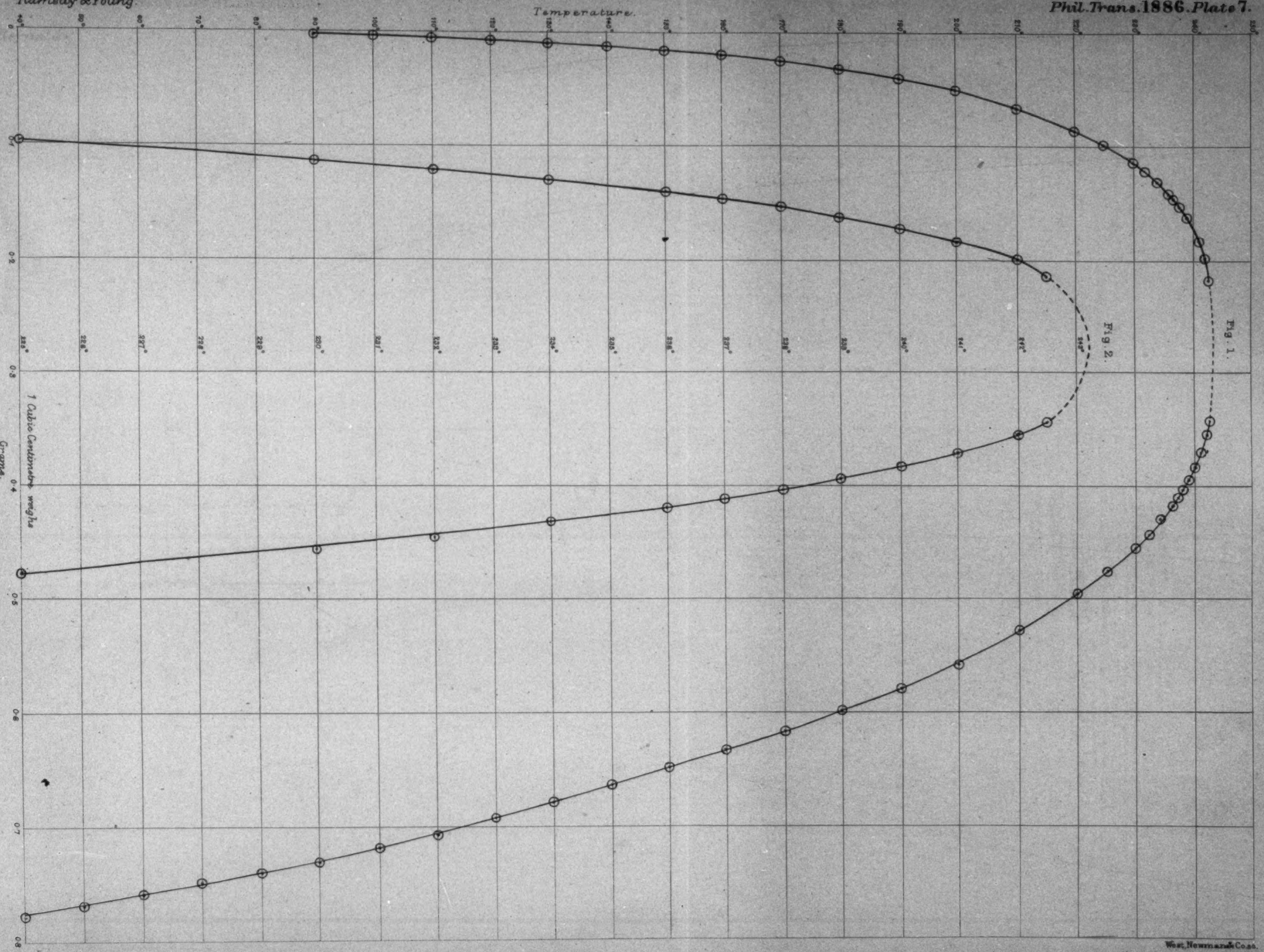


West, Newman & Co. sc.

Fig. 3.

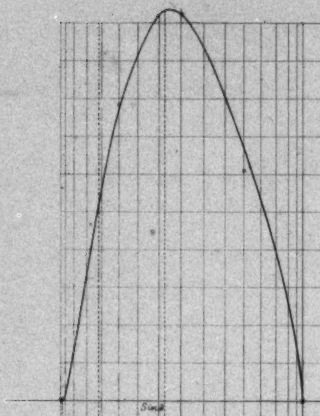
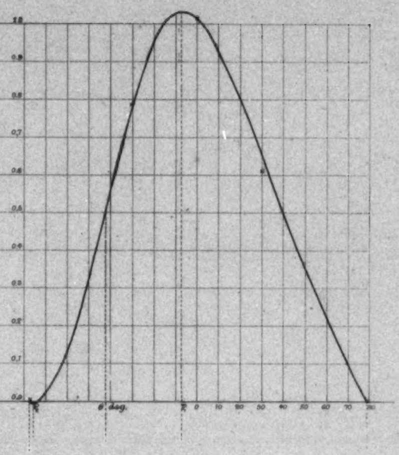


Fig. 2.



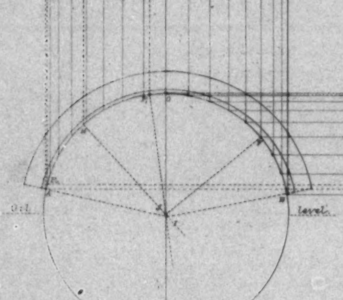


Fig. 1.

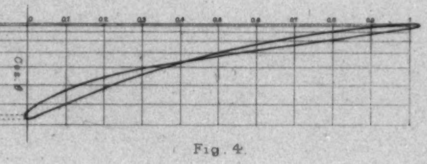


Fig. 4.

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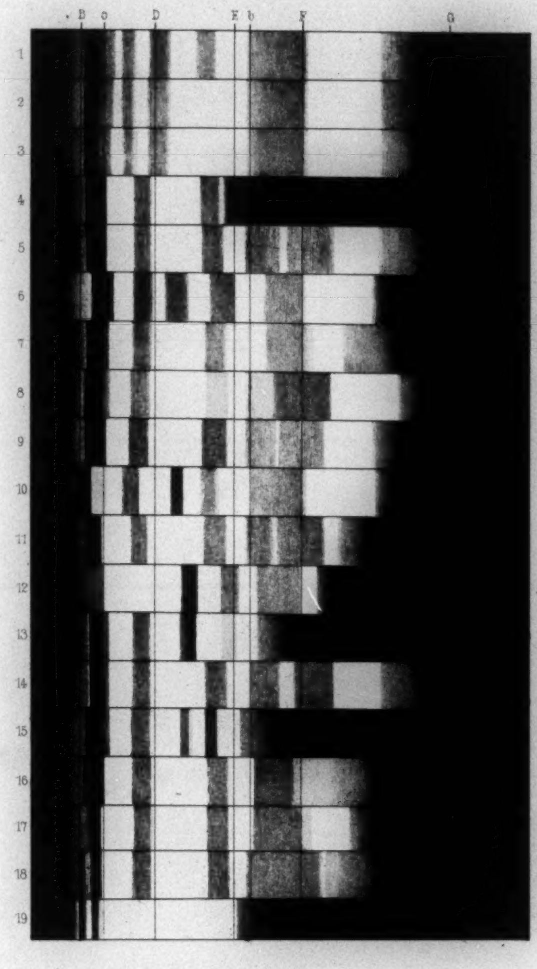

Chart I.

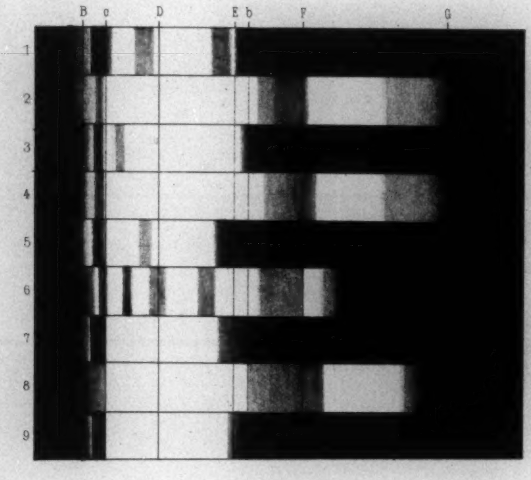

Chart III.

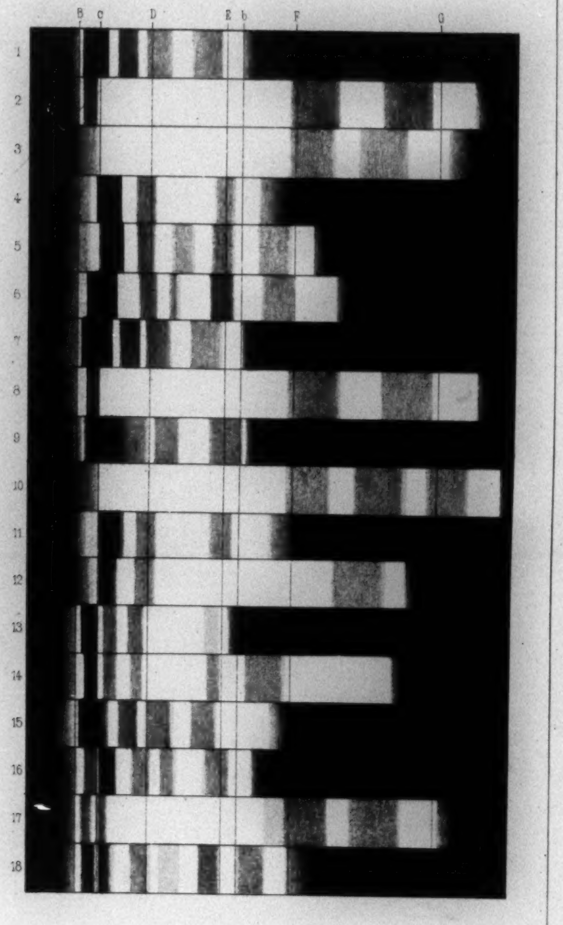

Chart II.

C. A. MAC MUNN ad nat del.

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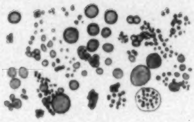

Fig. 1. x 320

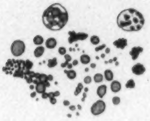

Fig. 2. x 320

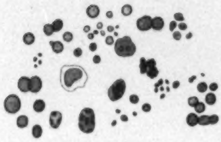

Fig. 3. x 320

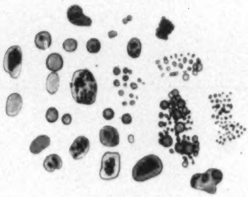

Fig. 4. x 320

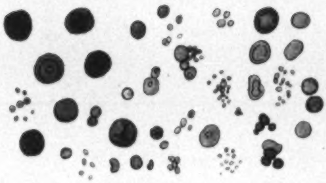

Fig. 5. x 320

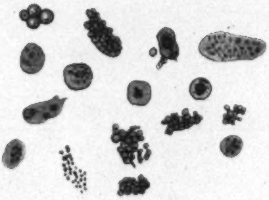

Fig. 6. x 320

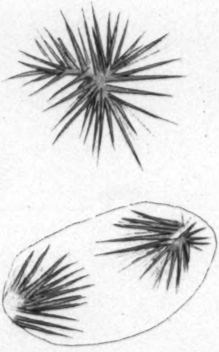

Fig. 7. x 320

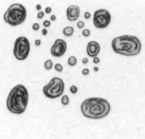

Fig. 8. x 320.

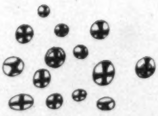

Fig. 9. x 320

C. A. MAC MUNN ad nat del.

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Mac Munn. Phil. Trans. 1886 Plate 11.

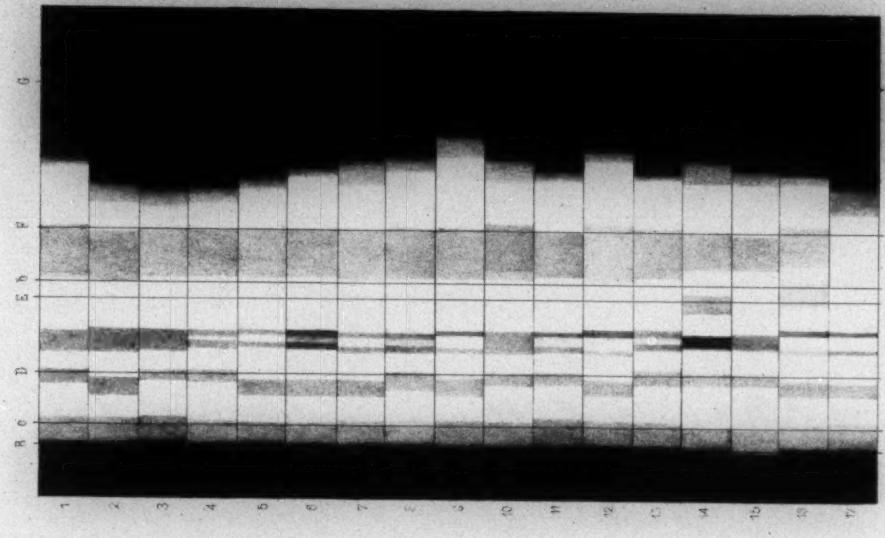

Chart II.

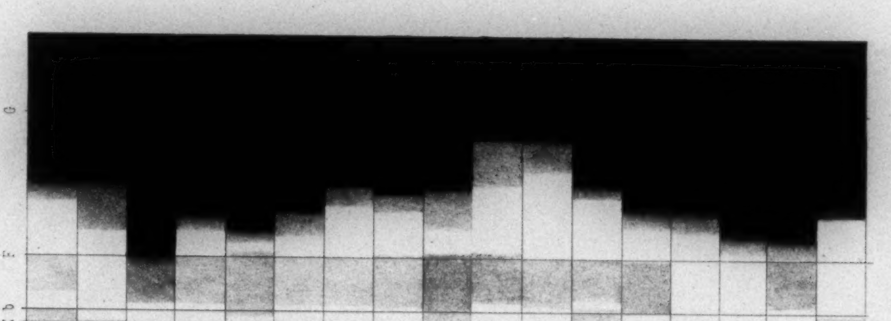

Chart I

C. A. MAC MUNN ad nat. del.

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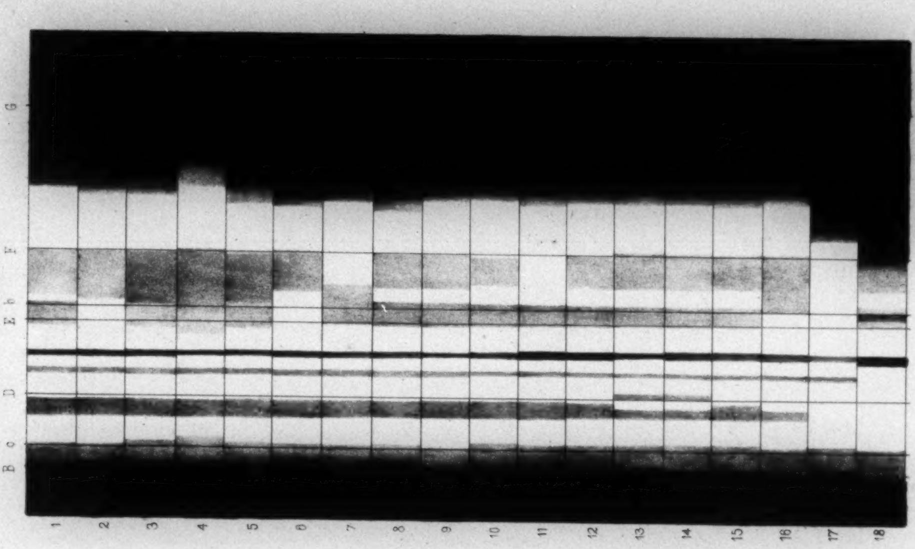

Chart IV.

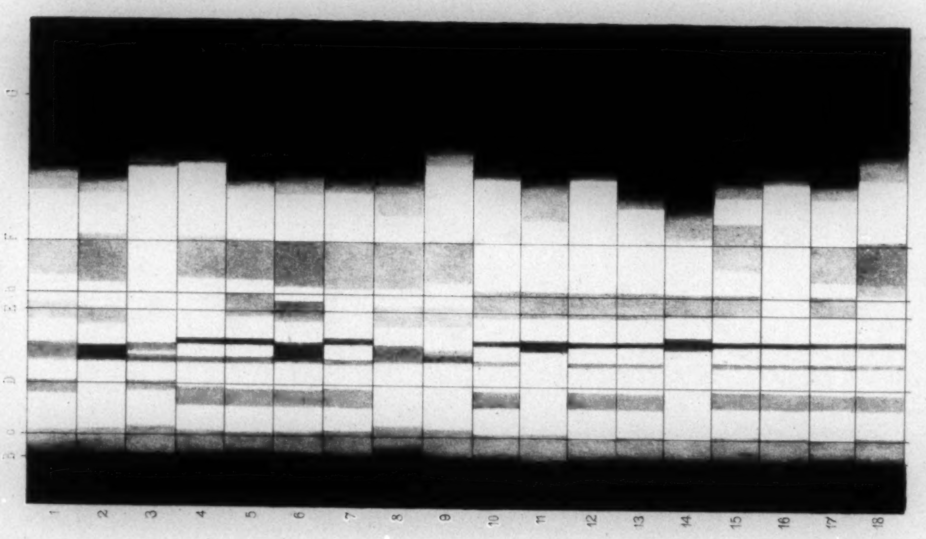

Chart III.

MAC MUNN ad nat. del.

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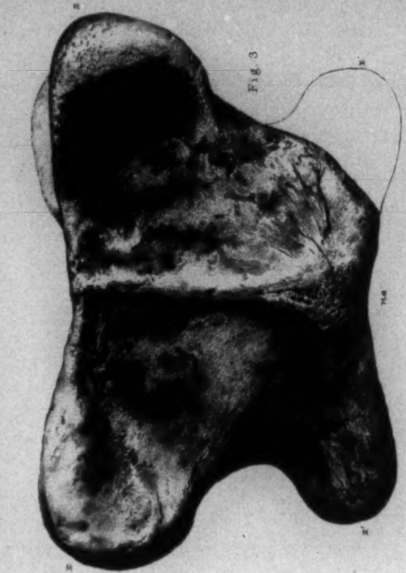


Fig. 3.

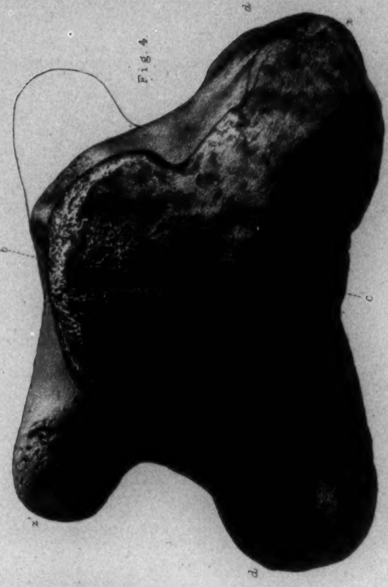


Fig. 4.

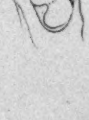


Fig. 2a.

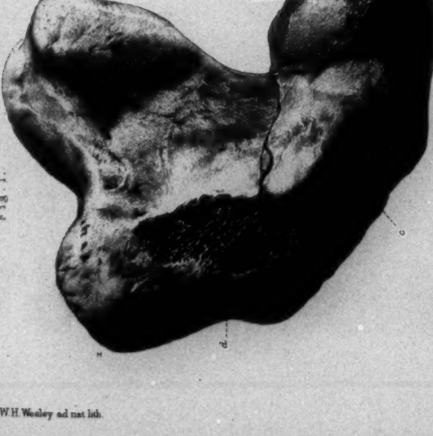


Fig. 1.

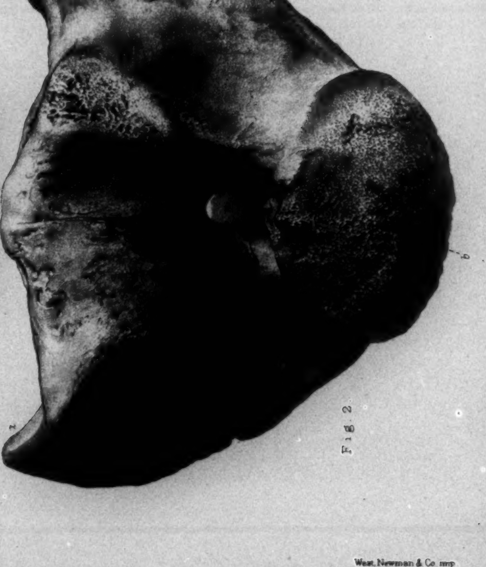
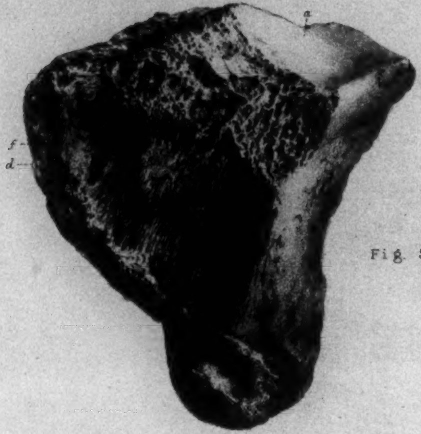


Fig. 2.

W. H. Wesley ad nat lith.

West, Newman & Co. imp.



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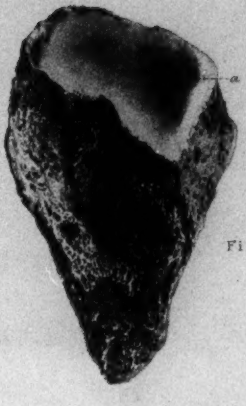
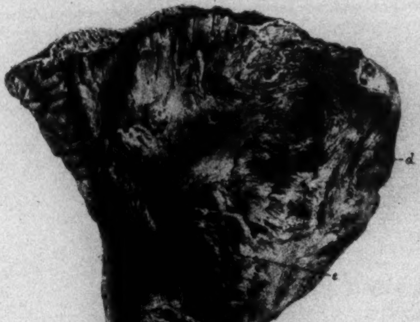


Fig. 6.

Fig. 7.



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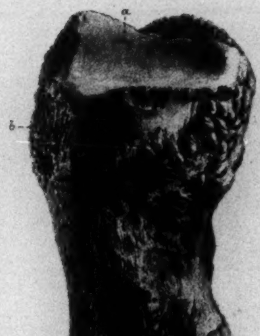

W.H.Wesley ad nat. lith.

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Fig. 10.

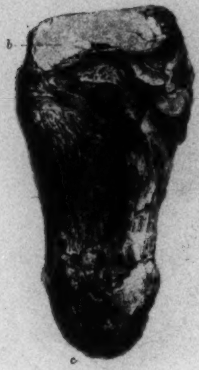
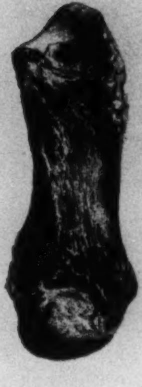


Fig. 11.



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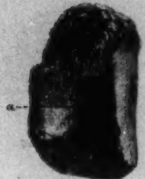

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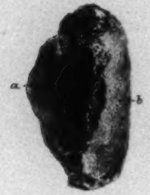
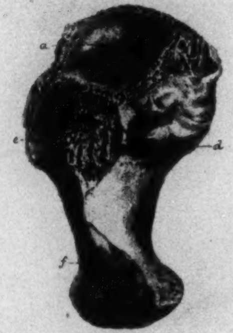


Fig. 13.



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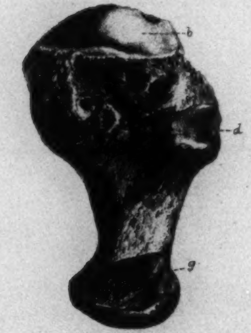
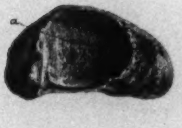


Fig. 17.



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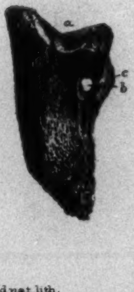


Fig. 19.

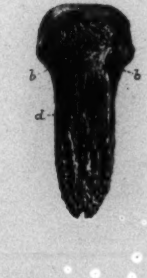
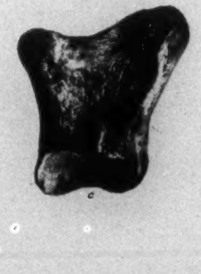


Fig. 16.



W.H. Wesley ad nat. lith.

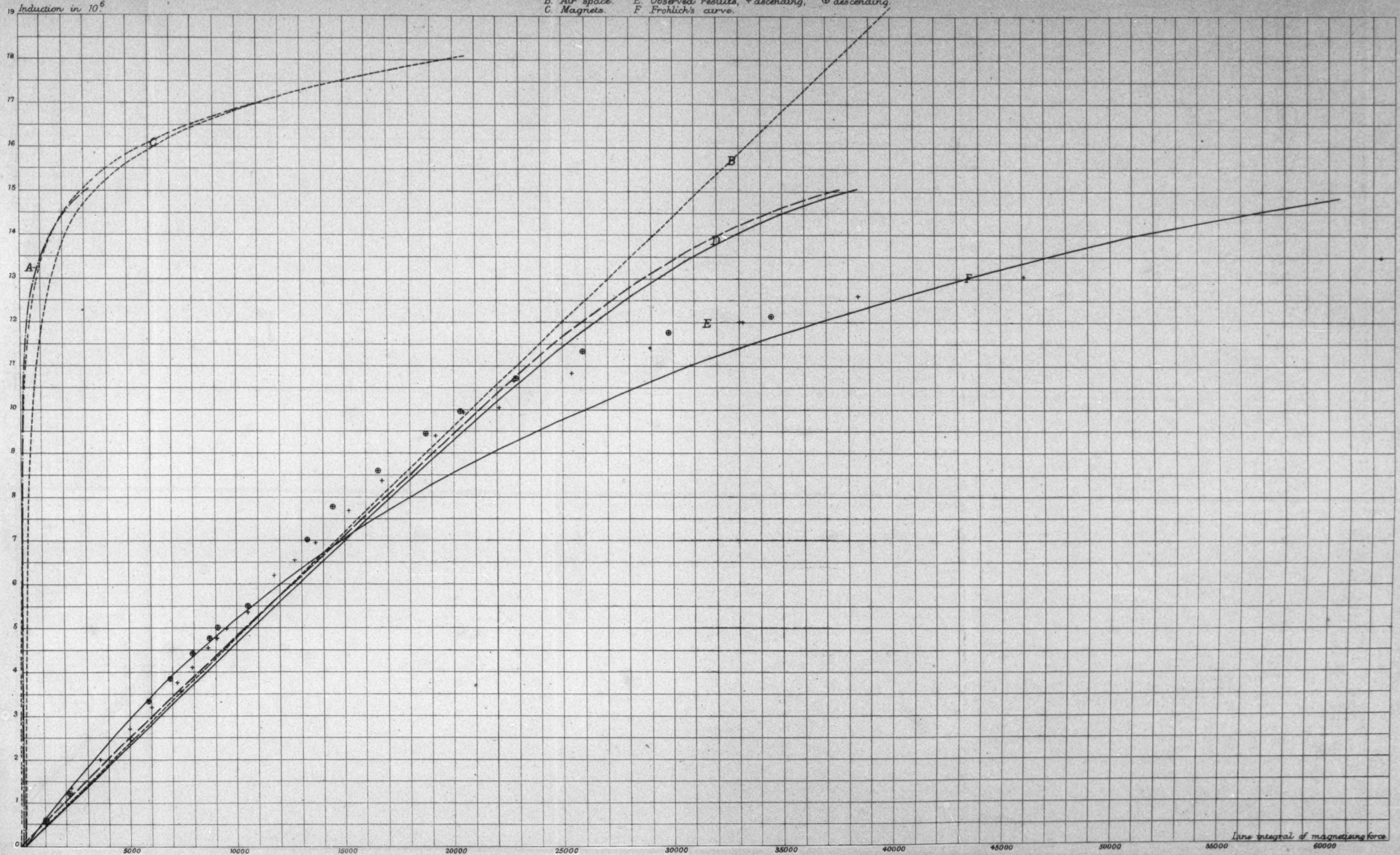
West, Newman & Co. imp.

J. & E. Hopkinson.

Sheet I.

Approximate Synthesis of characteristic curve.

A. Armature. D. Deduced curve.
B. Air space. E. Observed results, + ascending, ⊕ descending.
C. Magnets. F. Frohlich's curve.



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Sheet II.

Correct Synthesis of characteristic curve.

A. Armature.
B. Air space.
C. Magnets.
D. Calculated curve.
E. Observations, + ascending, ⊕ descending.
G. Yoke.
H. Pole pieces.

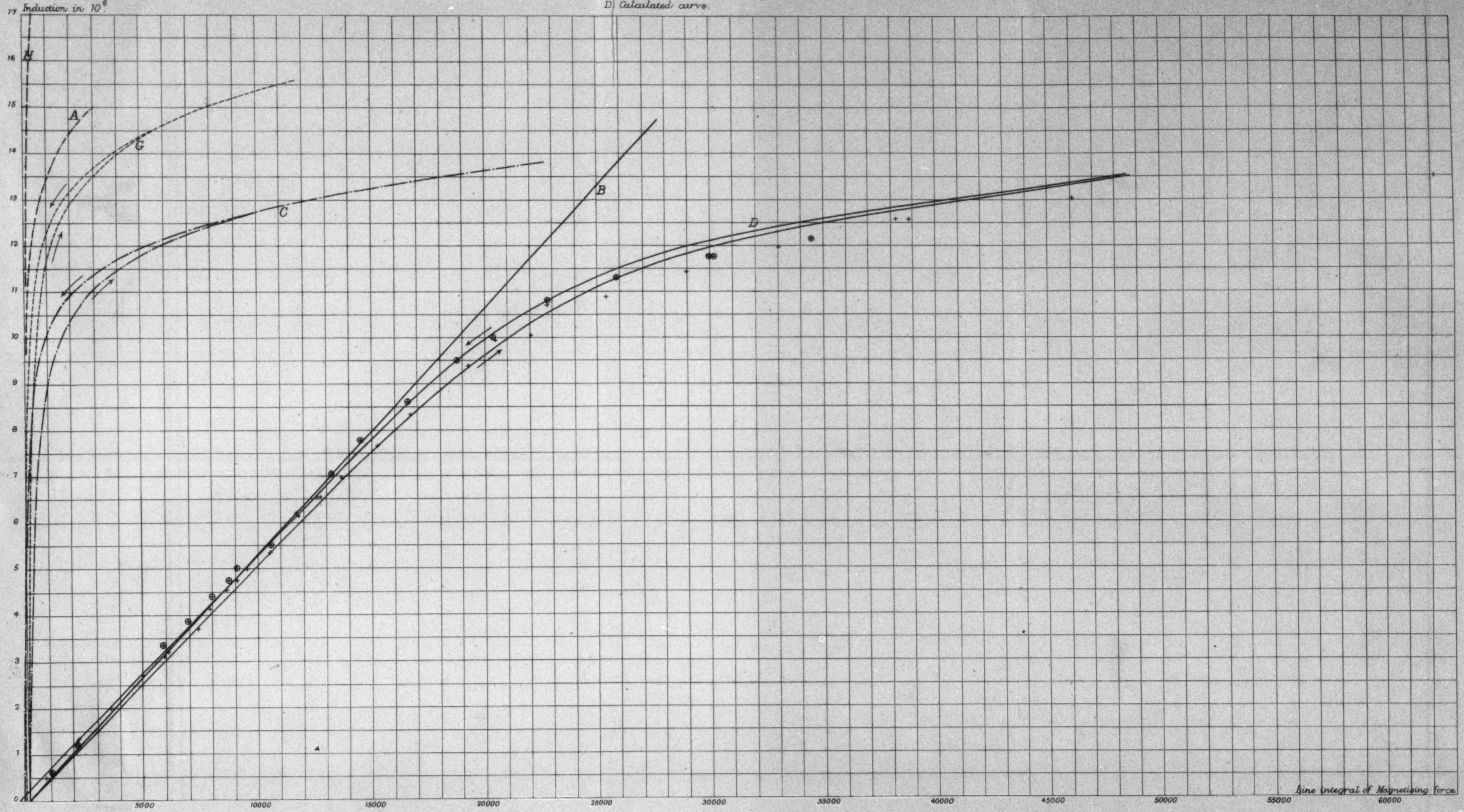

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Fig. 3.

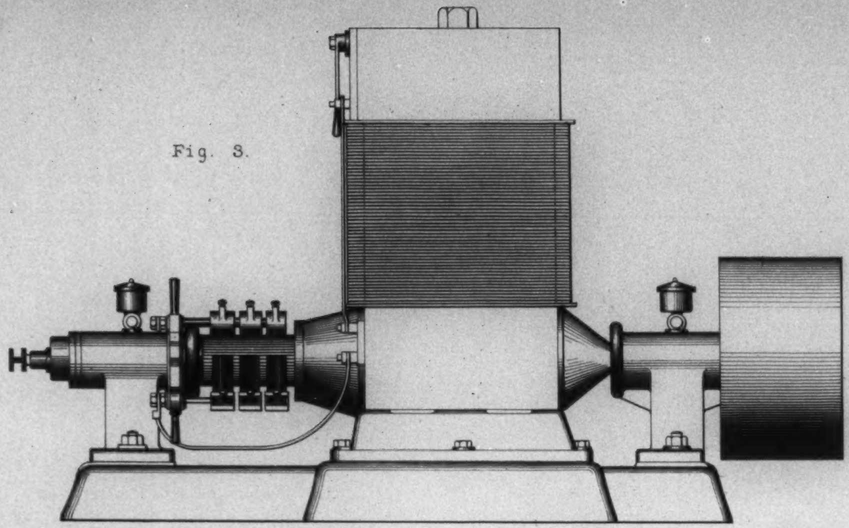


Fig. 4.

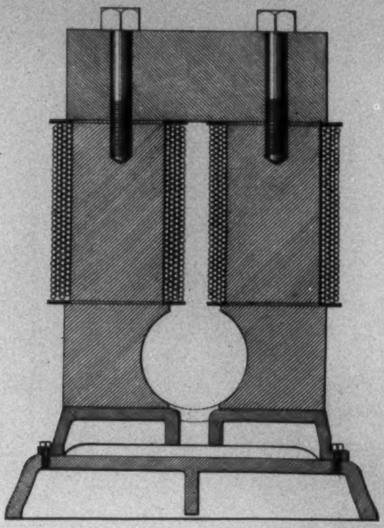
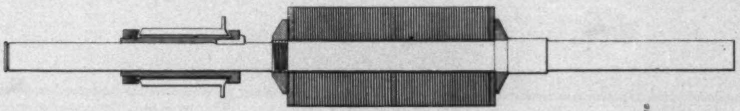
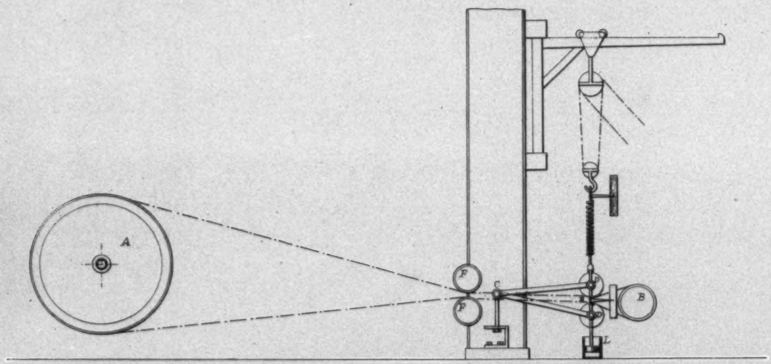
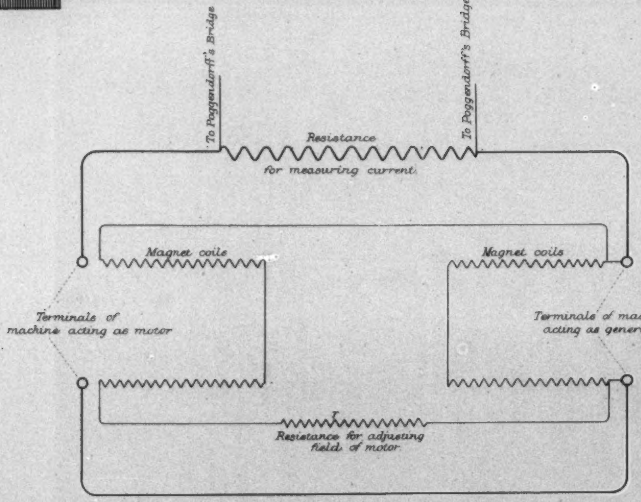


Fig. 5.





Scale, 1" = 1 Foot.


To Poggendorff's Bridge
To Poggendorff's Bridge
Resistance
for measuring current.
Magnet coils
Magnet coils
Terminals of machine acting as motor
Terminals of machine acting as generator
r
Resistance for adjusting field of motor.

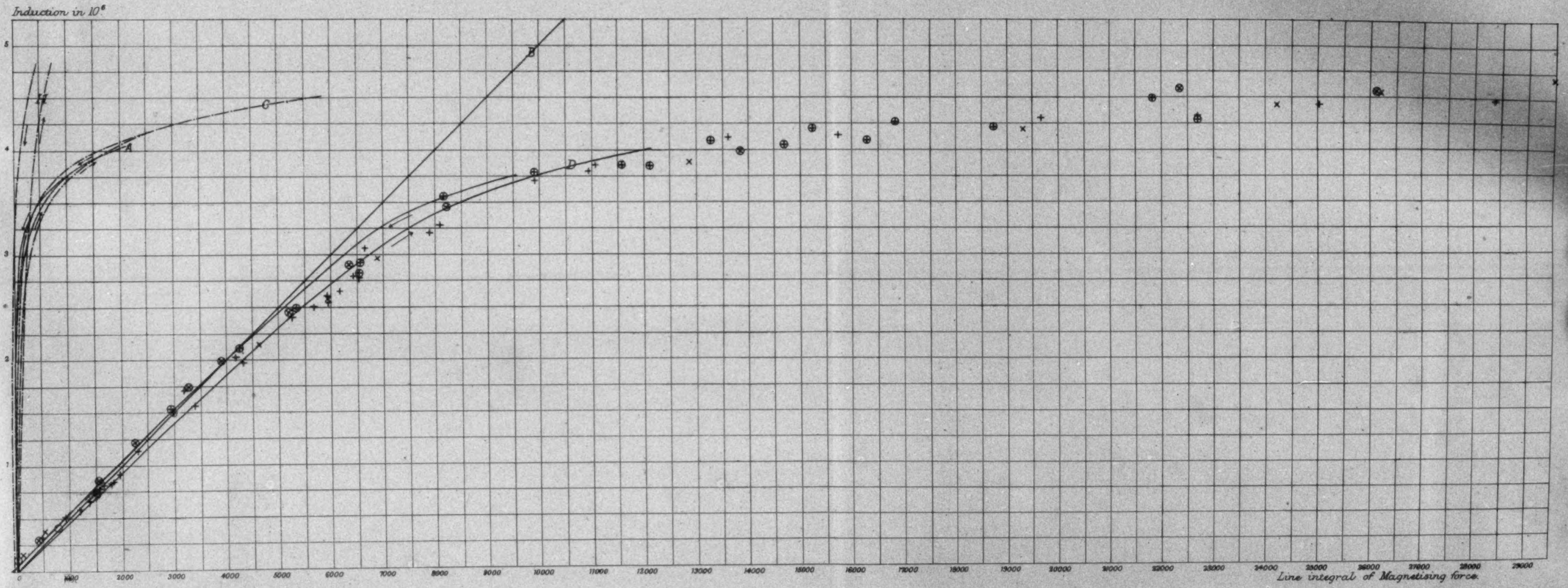
West, Newman & Co. lith.

Sheet III.

Synthesis of characteristic curve of Machine with Gramme armature.

Observed results { Nº 1 Machine + ascending ⊕ descending.
Nº 2 Machine × ascending ⊗ descending.

A. Armature.
B. Airspace.
C. Magnets.
D. Deduced curve.
H. Pole pieces.



West, Newman & Co. lith.

Fig. 1.

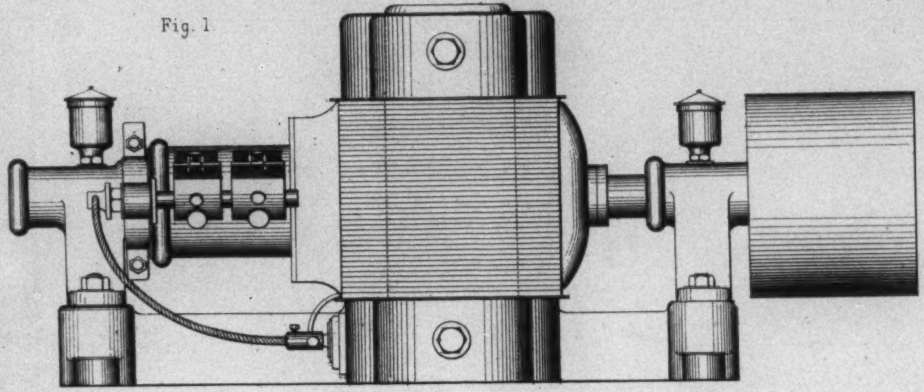


Fig. 2.

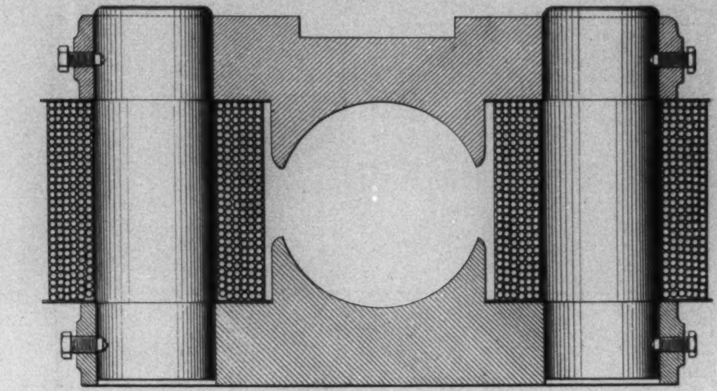
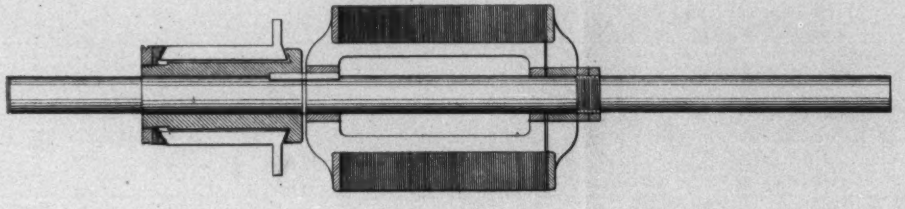


Fig. 3.



Scale ¼ full size.

West, Newman & Co. lith.

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